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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on page 3 of the Journal cover. New tables will be announced from time to time as they become available.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1406

Part of Journal of Research of the National Bureau of Standards, Volume 27, August 1941

QUANTITATIVE DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

By Dirk H. Brauns

ABSTRACT

It was found that certain organic fluorine compounds, including those which are easily volatilized at room temperature, can be quantitatively analyzed for fluorine by determining the loss in weight of a tared Pyrex flask caused by the etching action of the generated hydrofluoric acid. The sample is completely destroyed by heating with small amounts of potassium nitrate in sulfuric acid solution.

The method is very simple and can be performed in 4 hours, requiring only five weighings and no expensive apparatus.

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I. INTRODUCTION

In the course of a current investigation of optical rotation and atomic dimension, it was found desirable that a simple method of quantitative determination of fluorine in organic compounds be made available. Numerous methods have been published and their number has increased rapidly in recent publications.

W. Bockemueller [1] has discussed the methods up to the year 1932 and has added a new procedure himself; but since 1932 many others have appeared. This increased effort to find a simple method can be explained by increased application of organic fluorine compounds. In fact, M. Mayor [2] also gives at the end of his study on the preparation of organic fluorine derivatives the variety of applications of these compounds, such as liquids for refrigerating machines, insecticides, plastics, dyes, solvents, etc.

II. SURVEY OF EXISTING METHODS

For the quantitative determination of fluorine in organic fluoro derivatives, a conversion must first be performed from the organic fluoro compound to an inorganic fluoro compound. In the case of nonvolatile compounds this conversion has been made mostly by ignition with sodium carbonate in a nickel or platinum crucible. For organic fluorine compounds which are easily volatilized at room tem-

[1] Z. anal. Chem. **91**, 81 (1932).
[2] Rev. chim. ind. Paris **49**, 2-10; 30-34; 64-74 (1940).

perature, as well as for those which are gaseous at room temperature, the bomb or platinum combustion tube has been applied, which requires elaborate manipulations with special apparatus. After the fluorine in the sample has been converted to inorganically bound fluorine, it is usually quantitatively determined by weighing as calcium fluoride. This method is not satisfactory, because calcium fluoride is appreciably soluble in the wash water, and elaborate precautions, time-consuming evaporations, filtrations, and ignitions are necessary before it can be weighed.[3] H. Ost [4] determines the fluorine in the unwashed calcium fluoride (which however, must be free from silica) by the loss in weight of a glass plate used as a cover for a platinum crucible. The plate is etched by the hydrofluoric acid generated from the calcium fluoride by sulfuric acid. The method of Ost has been used by B. Helferich and R. Gootz [5] for determining the fluorine directly in nonvolatile organic fluorine derivatives. Thus the intermediate separation of calcium fluoride is unnecessary.

The investigation of the possibility of applying this simple etching process directly to volatile organic fluorine compounds has resulted in the new method described in this paper.

III. DESCRIPTION OF THE NEW METHOD

A flask of about 30-ml capacity with a small cup sealed at the flat bottom and a ground stopper of special design, as illustrated in figure 1, all made of Pyrex glass, is used in the determination. The flask is thoroughly cleaned with a hot solution of potassium bichromate in sulfuric acid, in which it is allowed to stand overnight, after which it is rinsed with distilled water and dried by drawing air through the warmed flask. Experiments showed that the flask thus cleaned can be heated to 300° C for 2 hours with pure sulfuric acid, or sulfuric acid with potassium bichromate, or sulfuric acid with potassium nitrate, without causing a decrease in weight of more than 0.2 mg.

The determination is made as follows: The stoppered flask is accurately weighed to 0.1 mg. A few small crystals of potassium nitrate (about 30 to 40 mg) are introduced in the flask outside the cup and about 8 ml of sulfuric acid is added to the same compartment by means of a long-stem funnel (*A*) and a 10-ml graduated cylinder. The stopper is greased with vaseline and placed upside down on the flask so that the orifice of the flask remains free from vaseline. The weight of the flask thus prepared is determined. The greased stopper is now placed aside, standing on the flat part so that no grease will be lost. The sample is introduced into the cup, using a funnel tube (*B*) for powders and a pipette in connection with the funnel tube (*A*) for volatile liquids. The curved tip of the funnel (*A*) can be used for tipping off the last drop to the wall of the cup, thus keeping the orifice clean. The greased stopper is used for closing the flask, and the new weight of the flask will yield the weight of the sample. This weight of the sample is regulated so that the decrease in weight of the flask, in milligrams, produced by the etching is approximately equal to the percentage of fluorine in the compound. This insures that the

[3] F. C. Hahn and E. E. Reid, J. Am. Chem. Soc. **46**, 1552 (1924). D. H. Brauns, J. Research NBS **18**, 322 (1937) RP978. Bockemueller, footnote 1.
[4] Ber. deut. chem. Ges. **26**, 151 (1893).
[5] Ber. deut. chem. Ges. **62B**, 2505 (1929).

weighing error shall not be more than 0.1 percent, when the weighings are made to 0.1 mg. After the flask is closed by the greased stopper and weighed and a rubber band hooked on to keep the stopper in place, the flask is rotated to mix the sample with the sulfuric acid. The flask is now placed in a 600-ml beaker filled with water, which is gradually heated to 70° C in the course of about one-half hour. The bath is regulated within this range for another one-half hour. Clamp-

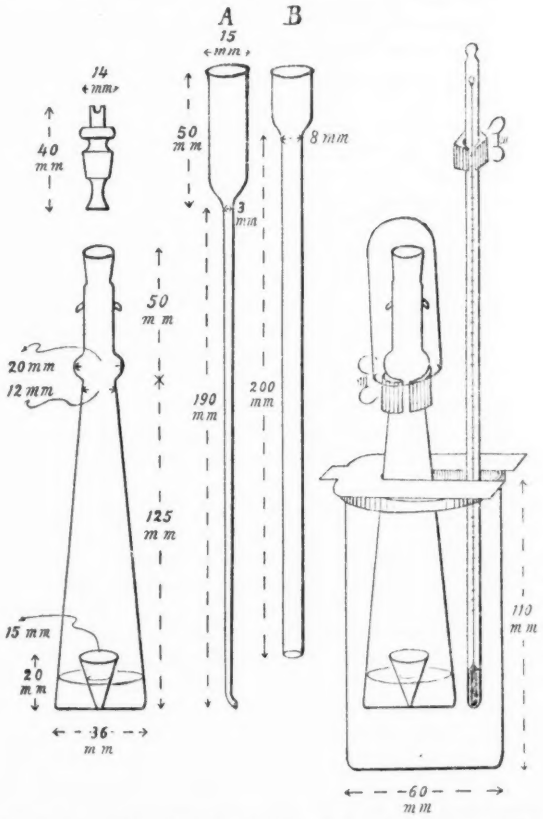

FIGURE 1.—*Quantitative fluorine determination apparatus.*

ing the flask in a stand is unnecessary if the flask is carefully handled and scratching avoided.

As the fluorine is strongly bound in 1-fluoro-2-methylbutane [6] and the compound is easily volatilized (boiling point 55.9° C), it is well-suited for a severe test of the new method. Hence, a detailed description of the fluorine determination in this compound follows. The procedure for nonvolatile fluorine derivatives could probably be shortened, but it seems advantageous to use the same method for all compounds. After the weighed sample is mixed with the sulfuric acid, as described above, one observes first that the 1-fluoro-2-

[6] D. H. Brauns, J. Research NBS **18**, 322 (1937) RP978.

methylbutane floats on top of the sulfuric acid. On warming, it gradually turns turbid yellow, and after one-half hour at 70° C all of the sulfuric acid has an even, transparent yellow-brown color. During this half-hour the flask is occasionally rotated so that a scrubbing action of the acid on the vapor in the neck is obtained (care being taken that the acid does not reach the stopper). The flask is now cooled in ice water or tap water. It will be noticed by removing the stopper that only little pressure exists in the flask, which indicates that there is no danger in heating to 60° to 70° C in the closed flask.[7] The open flask is now clamped in a stand and heated in an air bath consisting of a Pyrex tube supported by an iron ring and closed at the top by a thin copper plate cut out to receive the flask and a thermometer (see fig. 1). The temperature is slowly raised to about 120° C, and small crystals of potassium nitrate are dropped into the flask in the course of three-fourths hour until about 0.3 to 0.4 g has been used, the color of the liquid changing gradually from dark brown to light yellow. When brown nitrogen peroxide (NO_2) vapors are visible above the liquid after mixing by agitating the flask, sufficient potassium nitrate has been used, and the heating is now gradually increased until the temperature reaches 300° C. An inverted tube is placed over the neck of the flask as inadvertent heating above 300° C may cause the acid upon reaching the boiling point of sulfuric acid (320° to 330° C) to spurt out. As a result of this heating, undecomposed substance adhering to the neck is refluxed to the body of the liquid. The flame is now taken away, and the tube is allowed to cool, slowly at first, then more quickly by removing the air bath.

The liquid will be water-white when cold and straw-yellow when hot (dissociation of N_2O_5) if sufficient potassium nitrate has been used. To make sure that all fluorine is liberated from the organic compound and that the action of the hydrofluoric acid is complete, the heating to 300° C and cooling are repeated once or twice (compare footnote 7). For obtaining a check on the completion of the action of hydrofluoric acid on the glass, the cooled sulfuric acid solution is poured (for temporary storage) into a platinum dish or a weighed Pyrex beaker,[8] the small amount of sulfuric acid solution remaining in the flask being immaterial. The flask and stopper are rinsed with water (using a soft brush for cleaning the neck), further with pure alcohol, and then with ether to remove all acid and vaseline. The flask and stopper are then dried by a current of air. The cleaned Pyrex vessel with stopper is now allowed to stand in the balance case for 15 minutes and weighed. The sulfuric acid solution that has been put aside is poured back into the flask and the heating to 300° C and cooling are repeated, after which the flask is again cleaned and dried and the weight again determined. The weight is usually found to be constant, or there is a decrease of around 0.4 mg. The total decrease in weight in grams, multiplied by 1.0526 (conversion factor for Pyrex glass) gives the number of milligrams of fluorine, from which the percentage of fluorine in the sample is calculated.

[7] The decomposition to carbon dioxide and water is not completed during this preliminary heating. The important point is that all hydrofluoric acid is split off by this treatment, or converted to nonvolatile carbon compounds, the greater part being combined at this stage with the sulfuric acid (see J. H. Simons, H. J. Passino, and S. Archer, J. Am. Chem. Soc. **63**, 608 (1941), the remaining part etching the glass.

[8] The beaker is weighed for detecting action of any hydrofluoric acid during storage.

IV. CONVERSION FACTOR FOR CALCULATING THE FLUORINE CONTENT

Ost (see reference 4) determined empirically the loss in weight of soft glass by etching, using weighed amounts of calcium fluoride. His results indicated a loss of 0.8 to 0.9 mg of glass for 1 mg of fluorine. Helferich and Gootz (see reference 5), using organic fluorine derivatives of sugars of known constitutions and applying the etching method of Ost, found an average of 0.85 mg loss of weight of soft glass for 1 mg of fluorine in the sample. Helferich applied slides such as are used in microscopic work for the etching. Ost applied small amounts of 78-percent sulfuric acid sufficient for wetting the sample, which was weighed in the platinum crucible. The crucible was covered with a tared cover glass and heated in a sand bath for 4 to 8 hours to 100° to 150° C, and at the end to a higher temperature until sulfuric acid vapors appeared. By repeating the procedure of Ost-Helferich with the nonvolatile fluoro-derivatives of sugars, using a platinum crucible with soft-glass covers, there was also found an average loss of weight of 0.85 mg.

It was realized, however, by the writer that not only the use of a different glass (e. g., Pyrex glass) should have an influence on the factor, but possibly also the experimental conditions under which the determination is made. Indeed, replacing the platinum crucible with a soft glass crucible of about the same size changed the factor. This is probably due to escape of hydrofluoric acid from the platinum crucible without acting on the cover glass. It may be mentioned that the changed factor now agreed accurately with the factor calculated for soft glass according to the method applied below for Pyrex glass.

For investigating the possibility of extending the Ost-Helferich method also to volatile fluoro-derivatives, a platinum-lined bomb containing a weighed glass plate was first used. Difficulties were met because of the peculiar behavior of noble metals under oxidizing conditions and the leakage which frequently occurs. Then a stoppered Pyrex flask was used in which a Pyrex weighing tube containing the sample could be opened; thus the sample was brought in contact with 10 ml of sulfuric acid in the flask and gradually decomposed by heating as potassium nitrate was added. For preventing scratching of the glass, the weighing tube was surrounded by platinum gauze or wire. Finally, the described apparatus and method were devised in which no platinum is used. Using fluoro-derivatives of known constitution, it was found that the factor for converting the loss of weight of Pyrex glass to the weight of fluorine is 1.053. We may apply a tentative theoretical calculation for obtaining a theoretical conversion factor as follows:

Using for the composition of Pyrex glass SiO_2, 81.0 percent; B_2O_3, 13.0 percent and 6 percent of basic oxides (see E. Wichers, A. N. Finn, and W. S. Clabaugh),[9] the amount of fluorine used for etching 1 mg of Pyrex glass is:

$$\text{for } SiO_2 \text{ (yielding } SiF_4) \quad \frac{0.81 \text{ mg}}{\text{mol. wt } SiO_2} \times 4 \times \text{at. wt of F} = 1.02 \text{ mg of F}$$

[9] J. Research NBS **26**, 537 (1941) RP1394.

for B_2O_3 (yielding BF_3) $\frac{0.13 \text{ mg}}{\text{mol. wt } B_2O_3} \times 6 \times$ at. wt of F = 0.18 mg of F

6 percent of basic oxides will yield sulfates. Hence, a 1 mg loss of weight of Pyrex glass should correspond to 1.02+0.18=1.2 mg of fluorine.

In conclusion, it is recommended that a blank test be made and that the conversion factor as found by the writer be checked by using a pure nonvolatile fluoro-derivative, such as fluoracetyl-glucose or -arabinose, which can be easily prepared with the aid of hydrofluoric acid now marketed in cylinders.

V. ANALYSES

The following is an example of the calculation of the fluorine in fluorotriacetylarabinose:

	Grams
Weight of empty flask+stopper (1st weighing)	42.5252
Weight of flask+greased stopper+H_2SO_4+KNO_3(2d weighing)	56.5391
Weight of flask+greased stopper+H_2SO_4+KNO_3+substance to be analyzed (3d weighing)	56.6851
Weight of substance to be analyzed	0.1460
Weight of flask+stopper after 1st etching (4th weighing)	42.5156
Weight of flask+stopper after 2d etching (5th weighing)	42.5156
Loss by etching (42.5252 minus 42.5156)	=0.0096

F=0.0096×1.053=0.0101 g of F.

Percentage of F=(0.0101/0.1460)×100=6.9.

Theory=6.82 percent of F for $C_{11}H_{13}O_7F$.

Table 1 gives the complete analytical data.

TABLE 1.—*Analytical data obtained in the quantitative fluorine determination*

Name of substance and formula	Weight of substance	Weight loss, first etching	Weight loss, second etching	Weight of fluorine, indicated	Percentage of fluorine—	
					Indicated	Calculated
	g	*g*	*g*	*g*		
Fluorotriacetylarabinose, $C_{11}H_{13}O_7F$	0.1460	0.0096	0	0.0101	6.9	6.82
Fluorotriacetylarabinose, $C_{11}H_{13}O_7F$	.1458	.0098	.0001	.0104	7.1	6.82
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.0894	.0180	0	.0189	21.2	21.09
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.0945	.0189	.0003	.0202	21.3	21.09
1-Fluoro-2-methylbutane, $C_5H_{11}F$	.1583	.0308	.0006	.0331	20.9	21.09

VI. DISCUSSION

It was found by experiment that the loss in weight of glass containers in which organic fluorine derivatives are destroyed with sulfuric acid and potassium nitrate under definite conditions of procedure and apparatus is a reliable basis for the quantitative determination of fluorine in these compounds. In spite of the fact that the factor for converting the loss in weight of Pyrex glass to fluorine is only slightly more than 1 (1.053), the method yields fairly accurate results. No filtrations or ignitions are necessary and no difficult manipulations are involved. This method of decomposition is not satisfactory preliminary to determining chlorine, bromine, and iodine in organic

compounds as silver halides; also the destruction of volatile organic fluoro-chloro compounds needs a more vigorous attack.[10]

The peculiarity of the easy destruction of organic fluorine derivatives by sulfuric acid and liberation of hydrofluoric acid has been well known to investigators in this field, and Paternò and Spallino[11] have based a simple qualitative test for fluorine on this property. The present investigation has shown that this property also can be used for a simple quantitative determination of fluorine, and can give accurate results even for volatile fluorine derivatives if they are decomposed first in a stoppered flask.

The author expresses his appreciation to E. O. Sperling, chief of the Glassblowing Shop, for his advice and skill in the construction of apparatus needed in the pursuit of the work.

WASHINGTON, June 17, 1941.

[10] Preliminary experiments with stable fluoro-chloro compounds (Freon CF_2Cl_2) have shown that it may be possible to determine the fluorine in these compounds by the loss in weight of a small quartz combustion tube. Thus the advantage of a simple determination of the loss in weight would remain. These experiments may be continued at a later date.

[11] E. Paternò and R. Spallino, Gaz. chim. ital. **37**, II, 309 (1907).

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1407

Part of Journal of Research of the National Bureau of Standards, Volume 27, August 1941

THERMAL EXPANSION OF CAST AND OF SWAGED CHROMIUM

By Peter Hidnert

ABSTRACT

Data were obtained on the linear thermal expansion of six samples of chromium (99.2 to 96.3 percent) at various temperatures between −190° and +707° C. The expansion curves indicated anomalies at low temperatures. These anomalies were reversible on heating and cooling. The temperature at which anomalous expansion occurs appears to decrease with decrease in the purity of the chromium. Hysteresis was not observed on heating cast or swaged chromium to 300° C and cooling to low temperatures. Exceptionally low average coefficients of expansion were found for temperature ranges in or near the anomalous regions. The average coefficients of expansion of the samples of chromium from 20° C to various temperatures between 100° and 700° C lie between 5.7×10^{-6} and 10.3×10^{-6} per degree centigrade.

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I. INTRODUCTION

In a recent publication, the author [1] [1] reported data on the linear thermal expansion of electrolytic chromium at various temperatures between −105° and +715° C. Electrolytic chromium was found to contract during the first heating, when hydrogen presumably was evolved. It was possible to obtain smooth expansion curves after repeated heating.

The present paper gives results of an investigation on the linear thermal expansion of cast and of hot-swaged chromium at various temperatures between −190° and +707° C.

II. MATERIALS INVESTIGATED

Table 1 gives the chemical composition and the density of the samples of chromium which were investigated. Sample 1343I was prepared by Westinghouse Electric & Mfg. Co., Pittsburgh, Pa.; samples 1284, 1356, and 1356I by Research Department, Westinghouse Lamp Division, Bloomfield, N. J.; sample 1443I by P. Hidnert and F. R. Caldwell of the National Bureau of Standards; and sample 1285 was prepared by the Union Carbide & Carbon Research Laboratories, Inc., New York, N. Y.

[1] Figures in brackets indicate the references at the end of this paper.

TABLE 1.—*Chemical composition and density of chromium*

Sample	Material	Chemical composition [a]						Density [b] at 25°C
		Cr	Fe	Si	C	Mn	N	
		Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*g/cm³*
[c] 1343I	Hot-swaged rod, 2 mm in diameter	99.2	0.01	0.29		0.05		7.07
[d] 1284	Hot-swaged rod, 3 mm in diameter	98.3	.7	.34	0.08	.06	0.014	7.196
1443I	Cast pieces	97.4	2.01	.54	.04			
[e] 1356	Hot-swaged rod, 4 mm in diameter	96.7	0.02	.53	.09	.02	.065	6.86
1356I	Pieces cut from same rod as sample 1356.							
1285	Cast bar, 9- by 9-mm cross section	96.3	.9	1.00	.53	.07	.03	6.974

[a] Determined by R. M. Fowler, C. P. Larrabee, and J. C. Redmond, formerly of the National Bureau of Standards. Possibly the major amount of the undetermined percentage is oxygen. Some of the low-carbon samples may contain aluminum.

[b] Determined by E. Hill and S. Alpher, formerly of the National Bureau of Standards. Density determination on sample 1343I was made before the expansion tests. Other density determinations were made after the expansion tests.

[c] Found to be magnetic by H. L. Curtis of the National Bureau of Standards.

[d] Nickel, not detected. Duplicate sample was found to be diamagnetic by H. L. Curtis of the National Bureau of Standards.

[e] Oxygen, 1.05 percent; hydrogen, not detected. The values for oxygen and nitrogen are probably low on account of the presence of some oxide which was not decomposed by vacuum fusion.

III. APPARATUS

Samples 1343I, 1443I, and 1356I were investigated at various temperatures between −118° and +707° C with the interferometer method [2] [2] of measuring thermal expansion. Each sample consisted of three pieces of chromium of nearly equal length. The lengths of samples 1343I, 1443I, and 1356I were 6.648, 8.380, and 7.470 mm, respectively. The temperatures between room temperature and −118° C were obtained by passing liquid air through a coil in the furnace.

The precision comparator type of thermal-expansion apparatus described by Souder and Hidnert [4] was used at various temperatures between −127° and +701° C for six tests on sample 1284 and six tests on sample 1285. Tests 1 to 4 of each sample were made with the oil bath shown at the extreme right of figure 1 of their publication. Figure 3 of the same publication shows a sample, sample holder, and contact fingers for the vertical observation wires used in the oil bath. Tests 5 and 6 of each sample were made with the white furnace shown at the left of figure 1 of the publication by Souder and Hidnert [4]. Figure 4 of their publication indicates the method used in mounting each sample in the furnace. The lengths of samples 1284 and 1285 were 298 and 300 mm, respectively.

The fused-quartz thermal-expansion apparatus described by Hidnert and Sweeney [5] was used for sample 1356 and for tests 7 and 8 of sample 1284. The length of sample 1356 was 170 mm. Sample 1284 was cut to a 201-mm length before use in this apparatus.

At each observation in each type of apparatus, the temperature was kept constant for a sufficiently long time to make certain that the sample had attained constant temperature.

[2] The agreement between the results obtained with the interferometer method and the precision comparator method indicates that tilting of the specimens in the interferometer, which has been investigated by Saunders [3], was not an appreciable source of error in the measurements reported here. Numerous other examples in the literature, which show good agreement between the interferometer method and other methods, also indicate that most of the measurements made by the interferometer method have been free from serious errors.

IV. RESULTS

Figures 1 to 6, inclusive, show the observations [3] obtained on the linear thermal expansion of the six samples of chromium. Each expansion curve was plotted from a different origin. The dotted

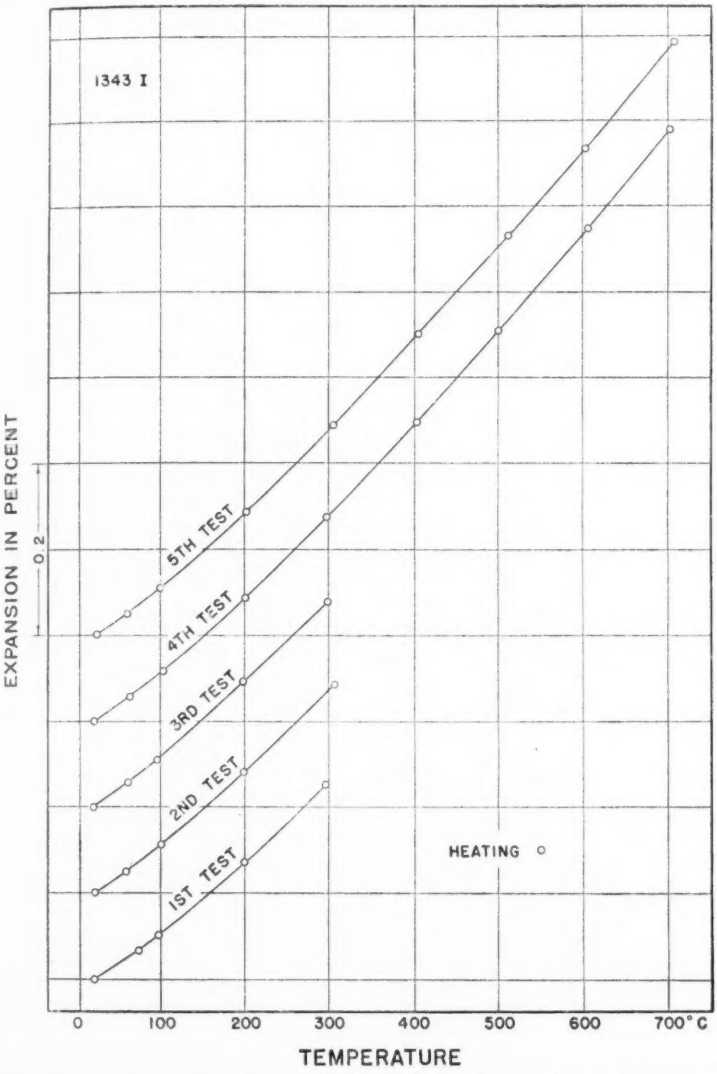

FIGURE 1.—*Linear thermal expansion of hot-swaged chromium, 99.2 percent.*

portions of two curves indicate that in these regions sufficient observations were not obtained to locate the curves definitely. All expansion curves in figures 1 to 6, inclusive, are convex toward the temperature axis, except those which will be indicated later.

[3] Some of the observations were omitted in order to avoid confusion. They were too closely spaced to be reproduced on figures of this size.

The observations obtained in five tests on heating the hot-swaged 99.2-percent chromium (sample 1343 I) to various temperatures between room temperature and 707° C are shown in figure 1.

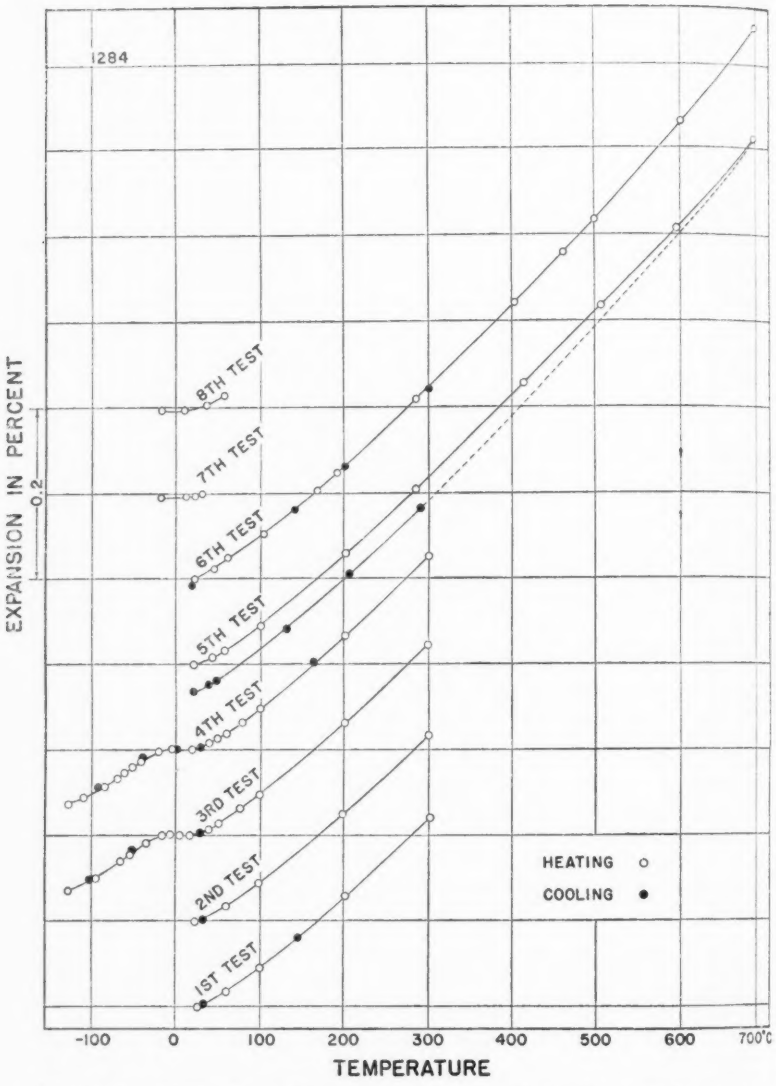

FIGURE 2.—*Linear thermal expansion of hot-swaged chromium, 98.3 percent.*

Figure 2 shows the observations in eight tests on the hot-swaged 98.3-percent chromium (sample 1284). In tests 1 to 4 between −127° and +303° C the solid circles representing the observations on cooling nearly coincide with the expansion curves. In the fifth test to 700° C the curve on cooling lies appreciably below the curve

obtained on heating. The observations on cooling in the sixth test over the same temperature range lie slightly below the expansion curve. The curves of tests 3, 4, 7, and 8 indicate anomalous expansion between −20° and +20° C. In this region the curves are nearly horizontal.

The observations obtained in three tests on cooling the cast 97.4-percent chromium (sample 1443I) are shown in figure 3. The curves indicate that this sample expands slightly on cooling between 0° and −20° C. The lower and the upper portions of the curves in the first test are practically straight. The curves in tests 2 and 3 are slightly concave toward the temperature axis.

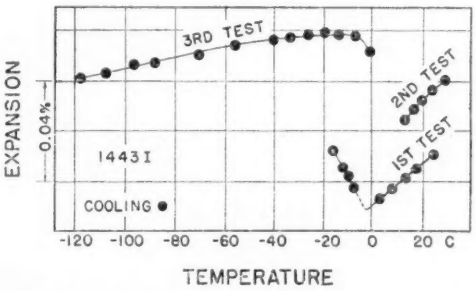

FIGURE 3.—*Linear thermal expansion of cast chromium, 97.4 percent.*

The observations obtained in a total of six tests on two samples of hot-swaged 96.7-percent chromium (samples 1356 and 1356I) at various temperatures between −190° and +702° C are shown in figures 4 and 5. A slight irregularity was noted near 0° C.

Figure 6 shows the observations in six tests on the cast 96.3-percent chromium (sample 1285). In tests 1 to 4 between −124° and +301° C, the solid circles representing the observations on cooling nearly coincide with the expansion curves obtained on heating. In tests 3 and 4 on cooling from about −30° to −50° C there was an expansion which was reversible on heating through the same temperature range. Below −50° C the curves are slightly concave toward the temperature axis. In the fifth test to 700° C the contraction curve lies appreciably below the expansion curve. In the sixth test to 700° C the observations on cooling lie slightly below the expansion curve.

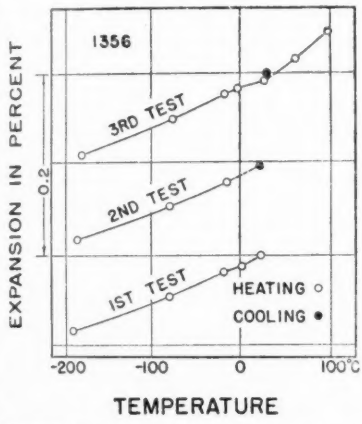

FIGURE 4.—*Linear thermal expansion of hot-swaged chromium, 96.7 percent.*

Average coefficients of expansion computed for various temperature ranges from the expansion and contraction curves are given in table 2. The last column of the table shows the difference in length before and after each expansion test indicated. The coefficients of expansion of sampels 1284, 1443I, and 1285 are exceptionally low in or near the regions where anomalous expansion was observed. In these regions the coefficients are, in some instances, negative.

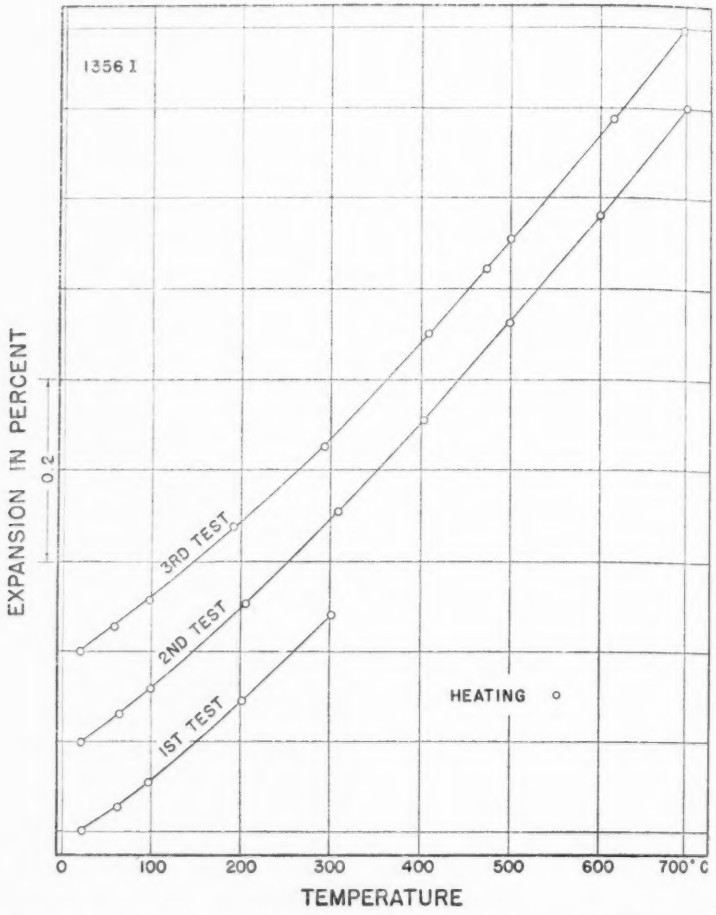

FIGURE 5.—*Linear thermal expansion of hot-swaged chromium, 96.7 percent.*

Table 3 gives a comparison of the average coefficients of expansion of the samples of cast and of swaged chromium in the present investigation with the average coefficients of expansion of electrolytic chromium obtained by the author [1] in a previous investigation. The average coefficients of expansion of electrolytic chromium for various temperature intervals between 20° and 700° C are within the ranges of the coefficients of expansion for the samples of cast and of swaged chromium.

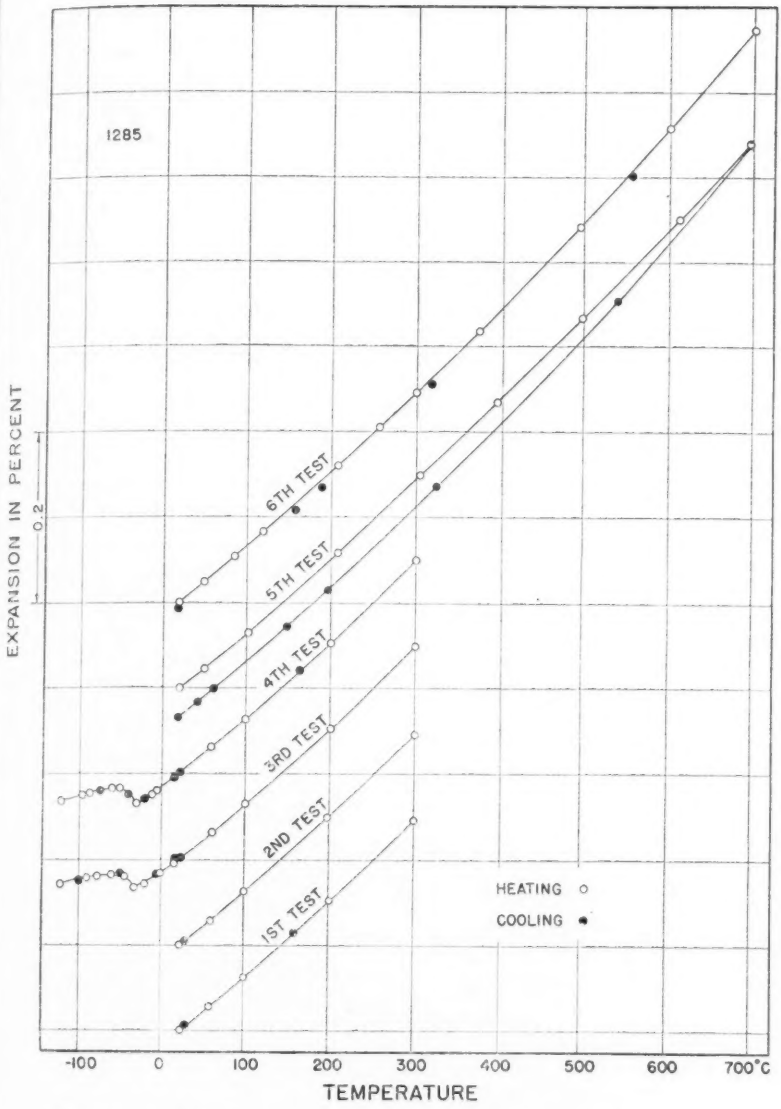

FIGURE 6.—*Linear thermal expansion of cast chromium, 96.3 percent.*

TABLE 2.—*Coefficients of linear expansion of chromium*

Sample	Material	Chromium content	Test [a]	Average coefficients of expansion. [The coefficients are obtained by multiplying the values in the table by 10^{-6}/°C]																							Change in length after heating and cooling [b]
				−190° to −20° C.	−190° to +20° C.	−125° to −100° C.	−100° to −50° C.	−50° to −15° C.	−15° to +20° C.	−20° to +20° C.	−80° to +20° C.	+20° to 60° C.	60° to 100° C.	100° to 200° C.	200° to 300° C.	300° to 400° C.	400° to 500° C.	500° to 600° C.	600° to 700° C.	20° to 100° C.	20° to 200° C.	20° to 300° C.	20° to 400° C.	20° to 500° C.	20° to 600° C.	20° to 700° C.	
		%																									%
1343I	Hot-swaged chromium	99.2	1H											8.5	9.4					6.8	7.7	8.3					
			2H									6.5	7.8	8.6	9.5					7.1	8.0	8.5					
			3H									7.1	7.6	9.0	9.3					7.3	8.3	8.6					
			4H									6.5	7.5	8.8	9.6	10.4	11.2	11.2	12.1	7.0	8.0	8.6	9.1	9.5	9.8	10.1	
			5H									6.8	7.8	8.7	9.7	10.6	10.7	11.3	11.8	7.3	8.1	8.6	9.2	9.5	9.8	10.1	
1284	Hot-swaged chromium	98.3	1H									5.0	6.9	8.4	9.1					6.0	7.3	7.9					0.000
			1C																	6.0							
			2H									4.4	7.2	8.2	9.0					5.8	7.1	7.8					−.001
			3H [c]			4.4	6.5	5.7	0.1			4.6	7.0	8.3	9.1					5.8	7.2	7.9					.000
			4H [c]			4.2	6.3	5.7	.3			4.6	6.9	8.5	9.3					5.7	7.2	8.0					.000
			5H									4.4	7.0	8.4	9.2	9.8	9.7	9.9	10.4	5.7	7.2	7.9	8.4	8.7	8.9	9.1	−.032
			5C									5.4	7.3	8.3	9.2					6.3	7.4	8.1				9.6	
			6H [c]									5.8	7.1	8.3	9.2	9.7	10.1	11.1	11.3	6.4	7.5	8.1	8.5	8.8	9.2	9.5	−.003
			7H							0.4																	
			8H							.3																	
1443I	Cast chromium	97.4	3C				2.0	[d]1.3																			
1356	Hot-swaged chromium	96.7	1H	3.8	3.9						4.4																
			2H	3.7	3.9						4.4																
			3H	4.1	3.9						4.1	6.6	8.1							7.4							
1356I	Hot-swaged chromium	96.7	1H									6.5	8.0	8.6	9.5					7.2	8.0	8.5					
			2H									6.8	7.8	8.8	9.9	10.5	11.3	11.6	11.9	7.3	8.2	8.8	9.2	9.7	10.0	10.3	
			3H									7.0	7.8	8.6	8.9	10.7	11.3	11.6	12.2	7.4	8.1	8.4	9.0	9.5	9.8	10.2	
1285	Cast chromium	96.3	1H [c]									8.2	8.4	9.0	9.3					8.2	8.7	8.9					+.002
			2H									7.8	8.6	8.8	9.4					8.2	8.6	8.9					.000
			3H [c]			2.6	1.1			7.2		8.0	8.4	8.8	9.6					8.2	8.5	8.9					−.000
			4H [c]			2.6	1.6			7.3		8.1	8.4	8.8	9.6					8.3	8.5	8.9					.000
			5H									7.7	8.2	8.8	9.4	9.4	9.8	10.0	10.6	8.0	8.5	8.8	9.0	9.2	9.3	9.5	−.033
			5C									8.0			9.5						8.5	8.8		9.3		10.0	
			6H									8.2	8.4	8.8	9.2	9.9	10.3	11.0	11.6	8.3	8.6	8.8	9.1	9.3	9.6	9.9	−.006
			6C												9.3						8.4	8.7				10.0	

[a] H indicates heating, and C, cooling.
[b] Determined from the expansion curve on heating and the contraction curve (or observation) on cooling. The plus sign indicates an increase in length and the minus sign a decrease in length.
[c] Observations on cooling close to expansion curve on heating.
[d] From −50° to −20° C.

TABLE 3.—*Comparison of coefficients of expansion of chromium*

Temperature range	Average coefficients of expansion	
	Samples of cast and of swaged chromium (99.2 to 96.3 percent)	Electrolytic chromium [a] (99.3 and 98.7 percent)
°C	$\times 10^{-6}/°C$	$\times 10^{-6}/°C$
20 to 100	5.7 to 8.3	6.8
20 to 200	7.1 to 8.7	7.4
20 to 300	7.8 to 8.9	8.0
20 to 400	8.4 to 9.2	8.5
20 to 500	8.7 to 9.7	8.9
20 to 600	8.9 to 10.0	9.2
20 to 700	9.1 to 10.3	9.5

[a] Computed from Hidnert's [1] eq 2.

Figure 7 shows the coefficients or rates of expansion, defined as $(1/L_{20})(dL/dt)$, at various temperatures between 40° and 650° C. The length of a specimen at temperature t is represented by L and its length at 20° C by L_{20}. The coefficients were derived from the average coefficients of expansion in table 2. Each vertical line at the

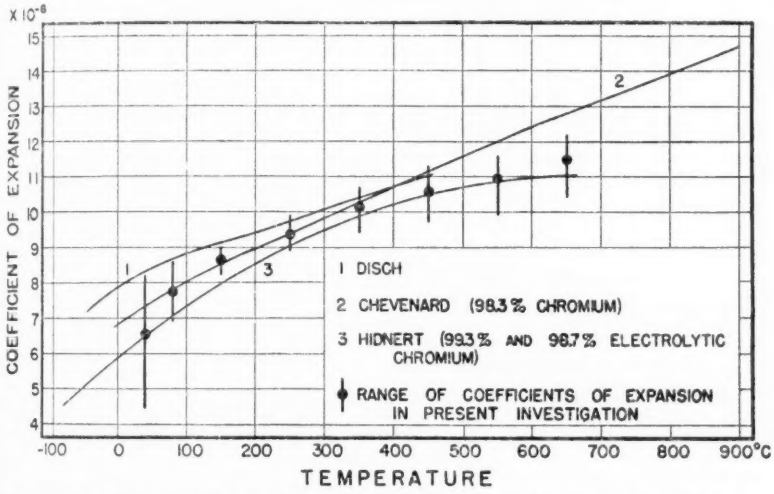

FIGURE 7.—*Comparison of coefficients of expansion (per °C) obtained in the present investigation on cast and on swaged chromium (99.2 to 96.3 percent) and in previous investigations by Disch [6], Chevenard [7], and Hidnert [1].*

temperatures indicated represents the range of the coefficients of expansion of the samples of chromium. The circle on each vertical line indicates the average of the coefficients of expansion at that temperature. This figure includes a curve derived from the data by Disch [6] on a sample of unknown purity, a curve from Chevenard [7] on a sample of chromium containing 98.3 percent chromium,[4] and a curve

[4] Impurities principally aluminum and iron, but amounts were not indicated by Chevenard.

from Hidnert [1] on two samples of electrolytic chromium (99.3 and 98.7 percent). A curve drawn through the circles representing the averages of the coefficients of expansion obtained in the present investigation at various temperatures from 40° to 650° C lies close to Chevenard's curve between 80° and 350° C and close to Hidnert's curve for electrolytic chromium at higher temperatures.

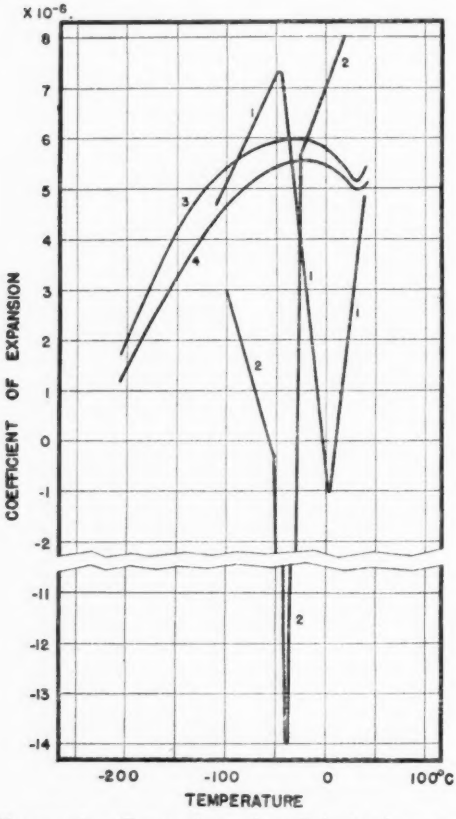

FIGURE 8.—*Comparison of coefficients of expansion (per °C) and anomalies in expansion of chromium obtained in the present investigation at low temperatures and in a recent investigation by Erfling* [8].

Curve 1.—Sample 1284, hot-swaged chromium (98.3 percent).
Curve 2.—Sample 1285, cast chromium (96.3 percent).
Curves 3 and 4 by Erfling [8] on sheet-rolled chromium and electrolytic chromium, respectively.

The curves in figure 8 indicate coefficients [5] of expansion of samples 1284 and 1285 at low temperatures. Two curves from Erfling [8] on rolled-plate chromium and electrolytic chromium of unknown purity are included in the figure. The four curves show anomalies in expansion. The curve for sample 1284 (98.3-percent chromium) shows a maximum at about −50° C and a minimum at about 0° C. The minimum of the curve for sample 1285 (96.3-percent chromium) is at about −40° C. Erfling stated that his curves for sheet-rolled chromium and electrolytic chromium show maxima at −30° and at −10° C, respectively.

V. DISCUSSION

Disch [6] appears to be the first investigator who reported an anomalous effect in chromium. He found that a sample of chromium contracted on cooling until the temperature reached about −183° C, but it expanded on further cooling. The contraction between +20° and −183° C was 1.25 mm/m, and that between +20° and −190° C was 1.0 mm/m. He was unable to obtain accurate values because the surfaces of the sample deformed at low temperatures.

The present investigation shows that the expansion anomaly in chromium is spread over a range of temperature and is not abrupt as in the polymorphic transition, or phase change, of iron at about 910° C. The anomaly is reversible on heating and cooling, without

[5] Derived from the original observations in the third and the fourth tests on heating and on cooling.

hysteresis. Bridgman [9] pointed out that phase changes in impure substances are spread over a range of temperature instead of being abrupt, but that phase changes in the presence of impurity are accompanied by hysteresis effects on account of the diffusion of the impurity from one phase to the other. As chromium does not show hysteresis, it appears that the anomaly does not represent a phase change.

Erfling [8] found that the rate of expansion decreased slightly from about −30° to +30° C for sheet-rolled chromium and from about −10° to +30° C for electrolytic chromium. Larger decreases in the rates of expansion were noted in the present investigation on two samples of chromium (see fig. 8). The rate of expansion of the sample of hot-swaged chromium (98.3 percent) decreased from about −50° to 0° C. The curve for the sample of cast chromium (96.3 percent) indicates that the rate of expansion decreased from −100° to about −30° C.

Anomalous effects in other properties of chromium have been observed by Bridgman [9] and Söchtig [10]. Bridgman's curve for the relative electrical resistance of a swaged rod of chromium plotted as a function of temperature shows an anomaly at about 10° C. He found no hysteresis between resistance and temperature (−80° to +80° C). He concluded that for those substances which do not show hysteresis, the mechanism responsible for the anomaly may be some intimate affair of the structure elements, and cannot be anything like those changes of lattice type that involve tearing down and building up again the lattice structure with comparatively large motions of some of the elements of the lattice or like anything else that involves motion of the elements of the structure through large distances.

Söchtig [10] investigated the electrical resistance of three samples of chromium. His curves show anomalies at about 40° C for electrolytic chromium and sheet-rolled chromium, and at −3° C for chromium of lower purity.[6] He also found no hysteresis in the electrical resistance with increasing and decreasing temperatures. In the temperature range of the anomaly, Söchtig found no change in the magnetic properties or in the structure of chromium. He concluded that the anomalous behavior of chromium cannot be ascribed to a change in the lattice structure but to the changes in the elastic forces between the atoms and the movement or attraction of the electrons.

Sasaki and Sekito [11] reported three crystalline forms of electrolytic chromium. They found that the hexagonal form is transformed at room temperature into the body-centered cubic form after 40 days from deposition, and that the form of the α-Mn type is also transformed into the body-centered cubic form after about 230 days. Wood [12] found that on heating the hexagonal structure of electrodeposited chromium a transition to the cubic form began at about 100° C and was complete at about 130° C.

The lack of hysteresis reported by Bridgman [9] and Söchtig [10] is confirmed by results of the present investigation between −190° and +300° C. Figures 2 and 6 show that the samples of chromium indicate hysteresis on heating to 700° C and cooling to room temperature.

[6] Purity of 3 samples of chromium not indicated by Söchtig.

As previous investigators failed to indicate the purity of the chromium samples on which anomalies were observed, it is not possible to correlate these anomalies with the composition. The results of the present investigation appear to indicate that the temperature at which anomalous expansion occurs decreases with decrease in the purity of the chromium.

Table 1 shows that the densities of the samples of chromium of the present investigation lie between 6.86 and 7.14 g/cm^3. From the lattice constants for the hexagonal form, the body-centered cubic form and the cubic form of the α-Mn type, Sasaki and Sekito [11] calculated the densities 6.08, 7.21, and 7.48, respectively. The observed densities are in closest agreement with the calculated density for the cubic form of chromium.

In view of the fact that chromium of various purities indicates anomalies at low temperatures, it appears that investigation of the properties of various chromium alloys at low temperatures may disclose other anomalous effects.

The author expresses his appreciation to the companies indicated in section II of this paper for the samples of chromium.

VI. REFERENCES

[1] P. Hidnert, *Thermal expansion of electrolytic chromium*, J. Research NBS **26**, 81 (1941) RP1361.
[2] G. E. Merritt, *The interference method of measuring thermal expansion*, BS J. Research **10**, 59 (1933) RP515.
[3] J. B. Saunders, *Improved interferometric procedure with application to expansion measurements*, J. Research NBS **23**, 179 (1939) RP1227.
[4] W. Souder and P. Hidnert, *Measurements on the thermal expansion of fused silica*, Sci. Pap. BS **21**, 1 (1926) S524.
[5] P. Hidnert and W. T. Sweeney, *Thermal expansion of magnesium and some of its alloys*, BS J. Research **1**, 771 (1928) RP29.
[6] J. Disch, *Über die Wärmeausdehnung einiger Stoffe*, Z. Physik **5**, 173 (1921); Wiss. Abh. physik.-tech. Reichanstalt **5**, 263 (1921).
[7] P. Chevenard, *Dilatabilité du chrome et des alliages nickel-chrome dans un intervalle étendu de températures*, Comptes rend. **174**, 109 (1922).
[8] H. D. Erfling, *Studien zur thermischen Ausdehnung fester Stoffe in tiefer Temperatur*, Ann. Physik **34**, [5] 136 (1939).
[9] P. W. Bridgman, *Compressibilities and pressure coefficients of resistance of elements, compounds, and alloys, many of them anomalous*, Proc. Am. Acad. Arts Sci. **68**, 27 (1932–33).
[10] H. Söchtig, *Untersuchungen an reinem Chrom im Anomaliegebiet*, Ann. Physik **38**, [5] 97 (1940).
[11] K. Sasaki and S. Sekito, *Three crystalline modifications of electrolytic chromium*, J. Soc. Chem. Ind. Japan **33**, 482B (1930).
[12] W. A. Wood, *Transition from hexagonal to cubic electrodeposited chromium*, Phil. Mag. **24** [7], 511 (1937).

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CHEMICAL REACTIONS OF THE CHLORITES WITH CARBOHYDRATES [1]

By Allene Jeanes [2] and Horace S. Isbell

ABSTRACT

Interest in the chemistry of the chlorites has recently been stimulated by the commercial production of sodium chlorite. Until just a few months ago the literature afforded only meager information about the general chemistry of the chlorites, and knowledge of their chemical behavior with the carbohydrates was limited to the fact that sodium chlorite bleaches the objectionable colored substances in paper and cotton textile materials without weakening the cellulose fibers. A reagent possessing the desirable properties of sodium chlorite should find extensive use in the field of carbohydrate chemistry. To provide a guide for the application of the reagent and to determine how the characteristic groups and structures occurring in the carbohydrates react with chlorites, the authors undertook a systematic investigation of the reactions of chlorites with carbohydrate material of diverse character.

This investigation has shown that at room temperature the nonreducing disaccharide, sucrose, is completely inert to chlorites under all conditions which do not involve acid hydrolysis, and that the ketoses, the polyhydroxy alcohols, and the aldonic acids are attacked only after treatment with chlorites for many days. In marked contrast to the glycosides, polyhydroxy alcohols, aldonic acids, and ketoses, the aldoses are oxidized readily and give the corresponding aldonic acids. The aldopentoses are oxidized more rapidly than the aldohexoses, and the monosaccharides more rapidly than the disaccharides. The reaction is slow in neutral solution but rapid in acid solution. Quantitative measurements under various conditions have revealed that chlorous acid is the oxidant and that the reaction corresponds in large measure to the following equation:

$$\underset{\text{(Aldose)}}{RCHO} + 3HClO_2 \longrightarrow \underset{\text{(Aldonic acid)}}{RCOOH} + 2ClO_2 + HCl + H_2O.$$

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[1] This paper was presented before the Division of Sugar Chemistry and Technology of the American Chemical Society at St. Louis, April 10, 1941.

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I. APPLICATION OF CHLORITES IN THE CARBOHYDRATE FIELD

Recently sodium chlorite has become commercially available and it has been advocated as a very useful bleaching agent for wood pulp and cotton textile materials [1].[3] The new reagent appears to oxidize and bleach the objectionable colored substances without materially altering or injuring the cellulose fibers. Aside from the bleaching action on cellulose very little was heretofore known concerning the reactions of chlorites with carbohydrate materials.[4]

The carbohydrates contain several characteristic groups which exhibit specific reactions with various oxidizing agents. Chlorine, bromine, hypochlorite, hypobromite, and hypoiodite react readily with aldoses to give the sugar acids or their lactones. On prolonged treatment with these reagents, the oxidation proceeds further and gives rise to lower acids, together with ketonic and dibasic acids. Oxidation of the ketonic group usually results in the cleavage of the carbon chain and the formation of lower acids. On oxidation with cupric acetate or phenylhydrazine, the sugars yield osones. Hydrogen peroxide, in the presence of iron salts, oxidizes the aldonic acids to the next lower sugars. Other reagents, such as periodic acid or lead tetraacetate, cause cleavage of the carbon chain and give dialdehydes. These examples clearly show that extensive generalization concerning the behavior of oxidizing agents with the carbohydrates cannot be made and that, in advance of this experimental study, the reactions of the new reagent could not be predicted.

In order to determine the behavior of chlorites with each of the constituent parts of a typical carbohydrate, a number of simple sugars and sugar derivatives were treated with chlorites in solutions of different acidity and the progress of the reactions was followed by determination of the optical rotation, acidity, and the amount of reducing sugar and chlorite. In these experiments, sucrose, methyl *α-d*-glucoside, mannitol, sodium gluconate, levulose, lactose, glucose, and arabinose were used to represent nonreducing disaccharides, the pyranosides, the open-chain polyhydroxy alcohols, aldonic acids, the ketoses, the reducing disaccharides, the aldohexoses, and the pentoses, respectively. These substances contain nearly all of the structural groups characteristic of the carbohydrates which might be used in conjunction with the new reagent.

Our results reveal that the glycosidic linkages in sucrose and in methyl *α-d*-glucopyranoside are not altered by chlorites, except in the presence of acid, which causes the well-known acid hydrolysis. Even after treatment for 105 days, neutral and alkaline sucrose solutions containing chlorites gave no indication of oxidation (see table 1). During the first 14 days samples of sodium gluconate and magnesium xylonate were not appreciably affected by chlorites; but on longer treatment small changes were observed. These observations clearly show the inertness of the carboxylic and the alcoholic groups of the carbohydrates to oxidation by chlorites. Levulose (table 2) was not appreciably affected by chlorites in the course of several days, but in 21 days some oxidation had occurred, as shown by a slight decrease in

[3] Figures in brackets indicate the literature references at the end of this paper.

[4] In 1939 M. C. Taylor, in conversation with one of us (Isbell), mentioned the production of sodium chlorite by the Mathieson Alkali Works and offered to supply some of the salt for investigation in the carbohydrate field. Shortly thereafter a sample, originally donated by the Mathieson Alkali Works, Inc., was obtained through the courtesy of A. L. Pitman, of the Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture.

reducing power. In marked contrast to the nonreducing carbohydrates and the ketoses, the aldoses are oxidized readily (tables 3 and 4). In subsequent paragraphs it will be shown that each aldose is oxidized to the corresponding aldonic acid and that the oxidation reaction provides a means for investigating the chemistry of chlorous acid.

TABLE 1.—*Behavior of nonreducing carbohydrates with chlorites in aqueous solutions at 20° C*

Time (days)	Sodium chlorite (5 g of $NaClO_2$ in 100 ml) pH=8.7 [a]		Sodium chlorite+sodium bicarbonate (5 g of $NaClO_2$+5 g of $NaHCO_3$ in 100 ml) pH=8.9 [a]		Calcium chlorite (4.3 g of Ca $(ClO_2)_2$ in 100 ml) pH=7.2 [a]		Sodium chlorite+sodium carbonate (4.8 g of $NaClO_2$+5.3 g of Na_2CO_3 in 100 ml) pH=10.1 [a]		Calcium chlorite+calcium carbonate (4.3 g of $Ca(ClO_2)_2$ in 100 ml+$CaCO_3$) pH=7.5 [a]		Sodium chlorite in acid solution [b] (5 g of $NaClO_2$+0.028 mole of H_3PO_4 in 100 ml) pH=2.2 [a]	
	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)
Sucrose (10 g of $C_{12}H_{22}O_{11}$ per 100 ml)												
0	+38.20	22.0	+37.80	22.0	+38.5	19.4	+36.50	21.4	+38.40	19.4	+36.40	[d] 22.2
1	+38.20	22.0	+37.80	22.0			36.70				+35.70	12.1
7	+38.20	21.9	+37.85	21.8	+38.35	19.1	+36.55	21.6	+38.70	19.1	+30.10	9.2
14	+38.17	21.9	+37.80	21.5			+36.65	21.4				
21	+38.35	21.8	+37.95	21.4	+38.30	19.6			+39.50	19.9		
49	+38.45	21.4	+37.70	21.3	+38.40	18.5			*+40.45	18.4		
105	*+39.60	18.9	+37.75	21.0								
Methyl α-*d*-glucopyranoside (10 g of $CH_3OC_6H_{11}O_5$ per 100 ml)												
0	+90.10	22.0	+90.40	22.0							+90.00	[d] 22.2
1	+90.10	22.0		22.0							+89.85	12.3
7	+90.20		+90.15	21.8							+89.75	9.2
49	+90.45	21.9	+90.15	21.3								
Mannitol (10 g of $C_6H_{14}O_6$ per 100 ml)												
0	Inactive	22.0	Inactive	22.0								
7		21.5		21.4								
14		*20.5		20.8								
49		16.9		20.1								
Sodium gluconate (12 g of $NaC_6H_{11}O_7$ per 100 ml)												
0	+8.00	22.0										
14	*+8.00	21.5										
21	+7.63	20.6										
49	+7.10	19.2										
Magnesium xylonate (11.4 g of $Mg(C_5H_9O_6)_2.5H_2O$ per 100 ml)												
0	+8.80	22.0										
14	+8.80	21.8										
21	+8.60	21.7										

[a] The pH values were measured at the beginning of the experiment.

[b] The samples were kept in sealed glass tubes.

[c] The values under this heading were obtained by titrating with $NaHSO_3$ solution the iodine liberated by treatment of the solution with potassium iodide and acetic acid, and they correspond to the sum of the chlorite, chlorous acid, and chlorine dioxide which remain in solution. Under the experimental conditions employed part of the chlorine dioxide escaped during the manipulations.

[d] The initial drop in the "titer" was caused by the loss of chlorine dioxide gas during the preparation of the samples. The "titer" at zero time was calculated from the amount of sodium chloride originally added. A control experiment run in the absence of any carbohydrate, using sodium chlorite, phosphoric acid and water in the proper proportions, gave the following results:

Time in days	0	1	3	5	7
"Titer" ml 0.1 *N* $NaHSO_3$/ml	(22.1)	12.2	10.9	10.6	9.6

[e] The slight rise in optical rotation was caused by slight evaporation of the solution over the long period of time.

[*] At this time the solution turned slightly yellow, which is evidence of the formation of ClO_2.

TABLE 2.—*Behavior of levulose with chlorites in aqueous solution at 20° C*

Time (days)	Sodium chlorite (5 g of $NaClO_2$ in 100 ml). pH=8.7 [a]			Sodium chlorite+sodium bicarbonate 5 g of $NaClO_2$+5 g of $NaHCO_3$ in 100 ml). pH=8.9 [a]			Calcium chlorite (4.3 g of $Ca(ClO_2)_2$ in 100 ml). pH=7.2 [a]			Calcium chlorite+calcium carbonate (4.3 g of $Ca(ClO_2)_2$+$CaCO_3$). pH=7.5 [a]			Sodium chlorite in acid solution [b] (5 g of $NaClO_2$+0.028 mole H_3PO_4 in 100 ml). pH=2.2 [a]		
	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* NaHSO/ml)
0	−54.51	101.7	22.1	−54.60	100.0	21.8	−55.40	103.3	19.4	−55.25	103.3	19.4	−53.95	98.0	[d] 22.2
1	−54.20	101.7	21.7	−54.50		21.1	−55.45		19.4	−55.15		19.4	−54.05	97.6	11.7
3	−54.05	99.6	21.2	−54.55	99.6	20.0		102.2					−53.85	96.0	10.8
7	−53.60	98.5	20.6	−53.60	99.1	18.5	−55.20	102.2	19.0	−55.30	102.2	19.0	−53.45	96.0	9.1
14	−53.50	101.2	20.9	−52.35	98.0	17.6	−54.45	102.2	19.1	−54.60	102.2	19.2			
21	−53.30	100.0	20.5	−51.10	95.8	16.0	−53.95	99.0	18.4	−54.20	99.0	18.9			

[a] [b] [c] [d] See corresponding footnotes, table 1.

TABLE 3.—*Reactions of aldoses with chlorites in aqueous solutions at 20° C*

Time (days)	Sodium chlorite (5 g of $NaClO_2$ in 100 ml) pH=8.7 [a]			Sodium chlorite+sodium bicarbonate [b] (5 g of $NaClO_2$+5 g of $NaHCO_3$ in 100 ml) pH=8.9 [a]			Calcium chlorite (4.3 g of $Ca(ClO_2)_2$ in 100 ml) pH=7.2 [a]			Calcium chlorite+calcium carbonate (4.3 g of $Ca(ClO_2)_2$+$CaCO_3$ in 100 ml) pH=7.5 [a]			Sodium chlorite in acid solution [b] (5 g of $NaClO_2$+0.028 mole H_3PO_4 in 100 ml) pH=2.2 [a]		
	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer [c] (ml 0.1 *N* $NaHSO_3$/ml)
d-Glucose (10 g of $C_6H_{12}O_6$ in 100 ml)															
0	+30.36	99.2	22.1	+30.02	99.8	22.0	+30.50	104.2	19.6	+30.50	100.8	19.6	+30.50	99.4	[d] 22.2
1	+30.15	101.5	22.0	+29.70		21.7	+30.65			+30.10		19.1	+21.90	70.3	14.0
2	+29.90		21.6		100.0		[e] +28.90	97.5	18.0	[e] +29.05	98.0	18.3	+21.05	69.9	12.9
4	[e] +28.43	98.4	20.3	+29.20		21.0	+25.45	87.6	13.7	+25.95	91.7	14.9	+20.05	69.0	10.2
7	+22.95	76.6	9.7	+29.00	100.0	20.5	+21.55	74.6	8.0	+22.10	76.3	8.7	+19.45	67.6	8.4
14	+18.25	68.1	2.7	+28.35	97.0	20.6	+18.98	71.5	5.3	+16.80	66.0	2.9			
21	+17.45	67.6	0.9	+27.90	97.0	20.3	+18.00	69.5	3.7	+14.73	61.8	0.9			

l-Arabinose (8.3 g of $C_5H_{10}O_5$ in 100 ml)

l-Arabinose (8.3 g of $C_5H_{10}O_5$ in 100 ml)

0	**+50.00	83.2	21.8	+50.00	83.2	21.8	**+50.00	83.2	19.3	**+50.00	83.2	19.3	+50.00	83.2	[d] 22.2
1	+29.35	51.1	10.9	*+38.43	65.3	14.5	+33.00	57.5	10.6	+33.15	57.8	10.1	+29.50	51.4	12.6
2	+26.20	46.9	8.1	+28.45	48.0	6.6	+28.70	51.1	8.3	+28.25	50.0	6.5			
3	+25.55	46.4	6.1	+24.60	41.4	3.4	+28.25	50.5	5.8	+26.70	47.6	5.0	+26.00	50.3	8.1
5	+24.50	44.7	3.8	+22.15	37.0	1.2	+27.45	48.8	4.1	+24.75	45.0	3.8	+21.35	46.3	6.4
7	+23.85	44.0	1.7	+21.40	34.4	0.5	+26.90	48.2	1.8	+23.50	42.3	2.8	+18.90	45.5	4.8

d-Xylose (8.3 g of $C_5H_{10}O_5$ in 100 ml)

0	+9.39	83.2	21.9	+9.45	82.6	22.0	+9.68	84.2	19.3	+9.68	84.2	19.3	+9.40	83.2	[d] 22.2
1	*+9.05	72.1	17.8	*+9.25	74.7	18.4	*+8.70	61.9	11.9	*+8.90	59.7	10.1	+6.35	53.0	12.9
2	+9.55	50.1	10.2	+9.32	56.1	9.9	+8.50	53.4	7.9	+8.63	52.9	6.3			
3	+9.10	48.8	8.0			4.6							+6.45	52.0	9.5
4	+8.65	48.1	6.2	+9.10	43.8	4.6	+7.80	52.6	7.0	+8.0	50.3	4.5	+6.90	50.0	8.2
7	+8.05	47.2	2.6	+9.00	37.4	1.6	+7.18	50.0	5.4	+7.25	46.0	3.3	+8.35	48.7	5.6
14	+7.75	46.7	0.5	+8.80	34.4	0.7	+6.75	49.0	2.7	+6.25	42.2	1.2			

Lactose (10 g of $C_{12}H_{22}O_{11}$ in 100 ml)

0	+32.10	98.0	22.1	+32.38	100.0	22.1		100.0	19.5		100.0	19.5			
1	+31.90	99.7	22.0	+32.05	99.1	21.7	+32.60			+32.45		19.4			
3	+31.80	99.9	21.6	+31.30	96.5	21.0	*+31.40	95.0	18.3	*+31.70	96.0	19.0			
7	*+29.85	92.5	20.0	+30.30	94.0	20.1	+29.25	82.9	15.8	+29.95	87.4	17.0			
14	+24.75	62.2	12.0	+29.15	90.3	20.0	+25.65	61.4	9.1	+26.40	64.0	10.8			
21	+21.15	46.8	4.3	+28.90	89.3	19.9	+23.85	51.4	4.7	+24.25	53.2	6.0			

[a],[b],[c],[d],* See corresponding footnotes, table 1.
** Color appeared in the solution after 1 hour.

TABLE 4.—*Oxidation of glucose at 20° C by chlorous acid in solutions of different acidities*

Saturated benzoic acid			0.56 *M* acetic acid			0.19 *M* phosphoric acid			0.56 *M* phosphoric acid		
0.056 mole *d*-glucose +0.056 mole sodium chlorite in 100 ml solution saturated with benzoic acid at 20° C.			0.056 mole *d*-glucose +0.056 mole sodium chlorite +0.056 mole acetic acid in 100 ml solution at 20° C.			0.056 mole *d*-glucose +0.056 mole sodium chlorite +0.019 mole phosphoric acid in 100 ml solution at 20° C.			0.056 mole *d*-glucose +0.056 mole sodium chlorite +0.056 mole phosphoric acid in 100 ml solution at 20° C.		
Time (min)	Optical rotation 2-dm tube (° S)	pH	Time (min)	Optical rotation 2-dm tube (° S)	pH	Time (min)	Optical rotation 2-dm tube (° S)	pH	Time (min)	Optical rotation 2-dm tube (° S)	pH
6.2	+29.35	4.2	5.3	+28.30	3.7	6.1	+25.74	3.2	5.9	+20.80	2.1
28.0	+27.89	4.6	15.3	+25.84	4.1	22.8	+25.00	4.0	15.0	+21.34	2.1
64.0	+26.87	4.7	30.3	+24.64	4.3	30.1	+24.68	4.1	24.8	+21.87	2.2
122.4	+25.78	4.8	133.0	+22.98	4.3	129.3	+24.50	4.8	178.4	+22.96	2.2
1,275.0	+21.97	4.9	1,394.0	+21.43	4.2	1,440.0	+21.78	3.8	1,414.0	+22.86	2.0
Sugar oxidized, 31.5 percent [a]			Sugar oxidized, 29.9 percent [a]			Sugar oxidized, 28.3 percent [a]			Sugar oxidized, 27.2 percent [a]		

[a] The percentage of oxidation was calculated from the reducing-sugar content at the time of the last sample.

II. OXIDATION OF ALDOSES WITH CHLORITES IN NEUTRAL AND ACID SOLUTION

The present investigation has revealed that under suitable conditions the aldoses are oxidized to aldonic acids by chlorites and that during the course of the reaction chloride, chlorine dioxide, and chlorate are produced. Inasmuch as the oxidation is slow in neutral and in alkaline solutions as compared with the oxidation in acid solutions, it appears that chlorous acid, or some substance derived therefrom, is the oxidant. Since chlorous acid decomposes spontaneously into chloride, chlorine dioxide, and chlorate,[2] these substances must be considered as possible oxidants in the aldose reaction. Previously Schmidt and Graumann [3] reported that several simple carbohydrates, including glucose, arabinose, levulose, and sucrose, were inactive in respect to aqueous chlorine dioxide. We have found (table 5) that the aldoses are oxidized slowly by chlorine dioxide and that in the absence of a buffer, sucrose is hydrolyzed. Nevertheless, the oxidation of aldoses by chlorine dioxide is very slow, and consequently, chlorine dioxide cannot be responsible for the rapid oxidation observed in solutions containing chlorous acid.

Other measurements (table 6) have shown that the aldoses are not oxidized by chloric acid or by chlorates and that neither of these substances can be the oxidant. Thus none of the products that are ordinarily formed during the decomposition of chlorous acid are particularly reactive, and it seems probable that the oxidation of the aldoses is effected by chlorous acid.

TABLE 5.—*Carbohydrates treated with chlorine dioxide in aqueous solution* [a] *at 20° C*

Time (days)	*l*-Arabinose (8.3 g of $C_5H_{10}O_5$ in 100 ml)			*d*-Glucose (10 g of $C_6H_{12}O_6$ in 100 ml)			Levulose (10 g of $C_6H_{12}O_6$ in 100 ml)			Sucrose (10 g of $C_{12}H_{22}O_{11}$ in 100 ml)	
	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Titer (ml 0.1 *N* $NaHSO_3$/ml)	Optical rotation 2-dm tube (°S)	Titer (ml 0.1 *N* $NaHSO_3$/ml)
0	+49.35	83.6	.....	+30.93	100.8	.....	−53.55	100.2	.....	[b]+38.40	.....
2	+47.50	80.8	14.2	+30.45	100.3	15.5	−53.20	100.2	13.7	+33.28	15.2
4	+46.00	79.1	10.1	+29.40	96.1	13.5	−51.42	99.0	14.3	+21.40	15.5
7	+43.00	76.3	8.8	+28.70	92.9	8.7	−52.10	99.0	12.1	+3.90	13.9

[a] The solutions contained approximately 3.3 g of ClO_2 per 100 ml and were kept in sealed glass tubes in the dark.

[b] The marked change in optical rotation is the result of inversion caused by acid formed from the chlorine dioxide.

TABLE 6.—*Carbohydrates treated with chlorates in neutral and in acid solutions* [a]

Time (days)	*d*-Glucose (10 g in 100 ml)			Levulose (10 g in 100 ml)			Sucrose (10 g in 100 ml)			*l*-Arabinose (8.3 g in 100 ml)	
	0.15 *M* $KClO_3$	0.15 *M* $KClO_3$, 0.56 *M* with acetic acid	0.15 *M* $KClO_3$, 0.56 *M* with phosphoric acid	0.15 *M* $KClO_3$	0.15 *M* $KClO_3$, 0.56 *M* with acetic acid	0.15 *M* $KClO_3$, 0.56 *M* with phosphoric acid	0.15 *M* $KClO_3$ —	0.15 *M* $KClO_3$, 0.56 *M* with acetic acid	0.15 *M* $KClO_3$, 0.56 *M* with phosphoric acid	0.15 *M* $KClO_3$	0.15 *M* $KClO_3$, 0.56 *M* with acetic acid
	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*	°*S*
0			+30.50				+38.40	+38.30	+38.15	+49.50	+49.50
1	+30.50	+30.65		−54.35	−54.35	−55.00					
7	+30.45	+30.65	+30.45	−54.36	−54.10	−54.80	+38.40	+29.50	−12.55	+49.15	+49.25
14	+30.40	+30.60	+30.45	−54.50	−54.35	−54.65	+38.50	+21.75	[b]−13.20	+49.40	+49.25

[a] Optical rotations in °*S*, read in a 2-dm tube, at 20° C.

[b] The optical rotation of a similar solution containing 10 g of completely hydrolyzed sucrose is calculated to be approximately −12.2°.

Investigation of the quantitative aspects of the reactions of the chlorites with the carbohydrates has been greatly complicated by the instability of chlorous acid. When one equivalent of a mineral acid is added to a cold aqueous solution containing sodium chlorite, the solution develops a yellow color which soon turns to reddish brown; on further standing, a yellow gas, presumably chlorine dioxide, is evolved and the solution becomes light yellow. Very little is known concerning the intermediate compounds necessary to explain these color changes. When an aqueous solution containing a chlorite and an aldose is acidified, the color changes previously noted for the chlorite alone are observed in somewhat more rapid sequence. An examination of the reaction in detail reveals that the oxidation of the aldose proceeds rapidly at first and then more slowly. After the initial rapid reaction the dark color, probably due to chlorous acid, disappears and the oxidation of the sugar virtually ceases, even though the solution contains both chlorine dioxide and chloric acid. The rapid initial oxidation reaction proceeds more rapidly in strongly acid solu-

tion than in less acid solution. Thus, as shown by the results given in table 4, when glucose is treated with sodium chlorite and phosphoric acid at pH 2.1, the reaction is substantially complete in 6 minutes, but at pH 4.2 the oxidation reaction continues over a period of several hours. Although the rate of reaction increases markedly with increasing acidity, the amount of oxidation produced by a given quantity of chlorite decreases slightly with increasing acidity. The smaller quantity of sugar oxidized in the more strongly acid solutions suggests that part of the chlorous acid undergoes a competitive side reaction and that the distribution of the chlorous acid between the competitive reaction and the carbohydrate reaction is influenced by the acidity. The existence of a competitive side reaction is in accord with the well-known decomposition of chlorous acid in acid solution.

According to the work of Taylor, White, Vincent, and Cunningham [1], the reaction of sodium chlorite with acetic acid at pH 2.5 produces chlorine dioxide and chloric and hydrochloric acids. When the solution is aerated to remove the chlorine dioxide as it is formed, the final products may be represented approximately by reaction I; but as suggested by Taylor, White, Vincent, and Cunningham, the chlorine dioxide and the chloric acid might be formed by separate reactions. Under suitable conditions chloric acid may be produced from chlorous acid by reaction II, or from chlorine dioxide by reaction III. In the presence of reducing agents, such as the aldoses, chlorous acid might be completely reduced to chloride (reaction IV), or it might be partially reduced and partially oxidized to give chloride and chlorine dioxide (reaction V). Since reactions I to V may take place simultaneously, interpretation of the oxidation process is a highly complicated problem.

$$4HClO_2 \longrightarrow HClO_3 + HCl + 2ClO_2 + H_2O \quad (I)$$

$$3HClO_2 \longrightarrow HCl + 2HClO_3 \quad (II)$$

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3 \quad (III)$$

$$\underset{\text{(Aldose)}}{2RCHO} + HClO_2 \longrightarrow \underset{\text{(Aldonic acid)}}{2RCOOH} + HCl \quad (IV)$$

$$\underset{\text{(Aldose)}}{RCHO} + 3HClO_2 \longrightarrow \underset{\text{(Aldonic acid)}}{RCOOH} + HCl + 2ClO_2 + H_2O \quad (V)$$

A better understanding of the course of the oxidation reaction can be derived from consideration of the quantitative relationships between the amounts of sugar oxidized and the reaction products. A summary of the results obtained by the treatment of glucose (1) with 3 moles of chlorous acid at 0° C, (2) with 1 mole of chlorous acid at 20° C, and (3) with one-half mole of calcium chlorite in a solution buffered with calcium carbonate, is given in table 7. In each case the reaction products correspond roughly to those required by the reaction of equation V. In the first experiment 1 mole of glucose consumed 3.83 moles of chlorous acid and gave in addition to gluconic acid, 1.35 moles of chloride, 0.47 mole of chlorate, and 2.01 moles of chlorine dioxide. According to reaction IV 1 mole of glucose would produce only 0.5 mole of chloride, while reaction V would result in the formation of 1 mole of chloride. Since more than 1 mole of chloride was isolated, it appears that reaction IV can be regarded as of little importance under the conditions of this experiment.

TABLE 7.—*Quantitative study of the products formed by the oxidation of glucose with chlorites in acid and in neutral solutions*

Constituents	I 0.0555 mole of glucose+0.1516 mole of $NaClO_2$+0.168 mole of acetic acid in 100 ml at 0° C for 24 hours	II 0.0555 mole of glucose+0.0531 mole of $NaClO_2$+0.056 mole of acetic acid in 100 ml at 20° C for 24 hours	III 0.0555 mole of glucose+0.0248 mole of $Ca(ClO_2)_2$ in 100 ml+$CaCO_3$ at 20° C for 7 days
	Moles	*Moles*	*Moles*
Chlorous acid consumed per mole of glucose oxidized	3.83	3.19	2.59
Chloride formed per mole of glucose oxidized	1.35	1.24	1.24
Chlorate formed per mole of glucose oxidized	.47	.14	.51
Chlorine dioxide lost per mole of glucose oxidized	2.01	1.82	.85
Oxalic acid formed per mole of glucose oxidized	none	none	.01

The utilization of more than 3 moles of chlorous acid per mole of glucose shows that the oxidation proceeds beyond the gluconic acid stage, or else that part of the chlorous acid was decomposed either by reaction I or by reaction II. The production of only 2 moles of chlorine dioxide per mole of sugar indicates that the excess of chlorous acid probably did not undergo reaction I, while the excess of chloride and chlorate found suggests that part of the chlorous acid was converted to chlorate and chloride by reaction II. It appears that in highly acid solutions the oxidation of glucose follows reaction V with small deviations, which may be explained by competitive reaction II. Chlorites in aqueous solution in the absence of reducing agents are stable for long periods of time. Hence the conversion of chlorous acid to chloric acid by reaction II does not take place readily in neutral solution, and under such conditions one might anticipate that very little of the chlorous acid would undergo decomposition. As a matter of fact, when the oxidation was conducted in neutral solution (experiment III) 1 mole of glucose reduced 2.59 moles of chlorite and gave in addition to gluconic acid, 1.24 moles of chloride, 0.51 mole of chlorate, 0.85 mole of chlorine dioxide, and 0.01 mole of oxalate. The quantity of chlorine dioxide separated in this experiment is much less than that required by reaction V. This discrepancy finds explanation in the chemistry of chlorine dioxide. Other experiments have shown that chlorine dioxide in aqueous solution in the presence of calcium carbonate is slowly decomposed according to reaction III. By this reaction 1 mole of chlorous acid and 1 mole of chlorate are formed from 2 moles of chlorine dioxide. Hence, if we assume that the chlorate found in the experiment under discussion is a measure of the amount of chlorine dioxide which had been hydrolyzed, we may calculate that the 0.51 mole of chlorate (determined by analysis) was derived from 1.02 moles of chlorine dioxide. By adding this quantity to that found experimentally, we may calculate that 1.87 moles of chlorine dioxide were produced. This compares favorably with the 2 moles required by reaction V. Furthermore, the hydrolysis of the chlorine dioxide would have produced 0.51 mole of chlorous acid, which would have been used in oxidation and would make the total chlorous acid used 3.10 moles in comparison with 3 moles required by reaction V. Thus the results in neutral solution may be explained by reaction V in conjunction with reaction III. The presence of a small quantity of oxalic acid among the oxidation

products shows that part of the sugar is oxidized beyond the aldonic acid stage, and this may account for the production of slightly more than 1 mole of chloride. Similar studies with *l*-arabinose and lactose revealed that in each case calcium aldonate, calcium oxalate, chloride, chlorine dioxide, and chlorate are produced. By comparison of the results obtained in neutral solution with those obtained in acid solutions, it will be noted that the reactions differ mainly in the reaction rates and in the relative importance of the side reactions II and III. In highly acid solutions reaction II is important, while in neutral and in slightly alkaline solutions reaction III is important.

The oxidation of aldoses with chlorites, even in neutral solution, appears to depend in large measure on the presence of chlorous acid. When an aldose is treated with a chlorite in neutral or slightly alkaline solution, considerable time elapses before a relatively rapid reaction begins. Ordinarily the oxidation does not become pronounced until after the lapse of several days, at which time the formation of chlorine dioxide is shown by the evolution of a yellow gas. The length of the induction period varies erratically with different sugars and with different samples of sodium chlorite. The end of the induction period is marked by the appearance of the yellow color caused by chlorine dioxide, and is accompanied by a significant increase in acidity. These observations confirm our conclusion that the oxidizing agent is chlorous acid. Presumably during the induction period the rate of reaction is slowly accelerated by the formation of chlorous acid, which oxidizes the carbohydrate and forms acids which in turn liberate additional chlorous acid and thus further increase the rate of oxidation.

Reference to table 3 shows that oxidations utilizing calcium chlorite exhibit a shorter induction period than those using sodium chlorite, either alone or in conjunction with sodium bicarbonate. Inasmuch as a freshly prepared aqueous solution of calcium chlorite is pale yellow and has the odor of chlorine dioxide. it must contain some free chlorous acid. In the concentrations employed in this investigation, solutions containing calcium chlorite have an initial pH of about 7.5. In table 8 it is shown that the rate of oxidation increases very rapidly as the pH of the solution falls below 8.

TABLE 8.—*Oxidation of pentoses with sodium chlorite in the presence of sodium bicarbonate*

Time (days)	*d*-Xylose				*l*-Arabinose			
	8.3 g of *d*-xylose+4.83 g of sodium chlorite+50 ml of sodium bicarbonate solution (saturated at 20°C) per 100 ml of solution				8.3 g of *l*-arabinose+4.83 g of sodium chlorite+50 ml of sodium bicarbonate solution (saturated at 20°C) per 100 ml of solution			
	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Sodium chlorite [a] (mg/ml)	pH	Optical rotation 2-dm tube (°S)	Reducing sugar (mg/ml)	Sodium chlorite [a] (mg/ml)	pH
0	+9.30	83.3	48.3	8.9	+49.85	83.3	48.3	8.9
3	+9.20	79.2	45.0	8.7	+46.95	78.0	44.4	8.7
7	+9.15	73.5	41.7	8.5	[b]+29.10	47.7	17.6	7.0
9	[b]+8.95	59.4	29.2	7.1	+21.70	33.0	5.1	7.1
11	+8.75	40.1	11.1	7.1	+20.30	32.6	3.1	7.6

[a] Any chlorine dioxide in the sample was removed by aeration with nitrogen, and the chlorite was determined by titration of the iodine liberated from potassium iodide in acetic acid solution.
[b] Indicates first appearance of yellow color in the solution.

It is of further interest to note the changes in acidity which accompany and follow the treatment of carbohydrates with chlorous acid. Samples of various sugars were permitted to react with sodium chlorite and phosphoric acid in sealed tubes, and at intervals the tubes were opened and the acidity was measured with a glass electrode. It will be observed from the data given in table 9 that in the absence of any carbohydrate or in the presence of sucrose or methyl α-*d*-glucoside, the acidity decreases from about pH 2.2 to about pH 2.8 and then increases to about pH 2.3. The initial decrease in acidity is caused by the formation of chlorine dioxide (reaction I), and the subsequent increase in acidity is caused by the slow hydrolysis of the chlorine dioxide with the formation of hydrochloric and chloric acids (reaction III). Presumably, in a closed system an equilibrium would be established between the chlorine dioxide, and the hydrochloric, chloric, and chlorous acids. In the experiments in which glucose, arabinose, and xylose were oxidized by chlorous acid, the acidity decreased rapidly to a minimum and then increased slowly. The initial decrease in acidity parallels the formation of chlorine dioxide and the rapid oxidation of the sugar, according to reaction V. The subsequent increase in acidity is presumably caused by the slow hydrolysis of the chlorine dioxide (reaction III). In this connection, it will be recalled that these experiments were conducted in closed tubes to prevent the loss of chlorine dioxide. After standing for 7 days, the acidity of the solutions containing oxidizable sugars was greater than the acidity of the solutions not containing easily oxidizable carbohydrates. The higher acidity found in the solutions containing oxidizable sugars arose from the formation of a larger quantity of hydrochloric acid and from the presence of aldonic acids formed in the course of the reaction. These remarks suffice to explain the observations, but it might be mentioned that part of the change in acidity may have arisen from the formation of sugar acid lactones and their subsequent hydrolysis.

TABLE 9.—*Changes in the acidity of carbohydrate solutions containing aqueous chlorous acid* [a]

Time (days)	Control (no sugar)	*d*-Glucose (10 g in 100 ml)	Levulose (10 g in 100 ml)	*l*-Arabinose (8.3 g in 100 ml)	*d*-Xylose (8.3 g in 100 ml)	Sucrose (10 g in 100 ml)	Methyl α-*d*-glucoside (10 g in 100 ml)
	pH	pH	pH	pH	pH	pH	pH
0	2.2	(b)	2.1	(b)	(b)	2.2	2.2
0.007		2.7		3.4	3.3		
0.021		3.4					
0.125	2.6	3.4		3.3		2.9	2.7
1	2.8						
3	2.7		2.6	2.0	2.2	2.7	2.7
5	2.6	2.1	2.3	1.8	1.8	2.4	2.4
7	2.4	2.0	2.2	1.7	1.6	2.2	2.3

[a] The chlorous acid was prepared from equal volumes of 1 *M* sodium chlorite and 0.5 *M* phosphoric acid. The samples were kept at 20° C in sealed glass tubes.

[b] This substance gave a rapid, exothermic reaction. The acidity at the beginning is presumably the same (pH 2.2) as that of the control experiment conducted in the absence of carbohydrate.

At the beginning of this investigation, it was thought likely that the ring modifications of the aldoses might be oxidized directly to lactones in a manner analogous to that previously observed in the oxidation of the aldoses with bromine water [4, 5]. Unfortunately,

the oxidation with chlorous acid in neutral solution is so slow that equilibrium between the delta lactones and the acids is established as the reaction proceeds, and although the oxidation in strongly acid solution is fairly rapid, the delta lactone under these conditions is also split rapidly. Thus, our measurements (changes in pH and in optical rotation) do not give information concerning the character of the oxidation product.

Inasmuch as the reducing sugars in solution contain a number of isomeric modifications in dynamic equilibrium, it is of interest to ascertain, if possible, the relative rates of reaction for the separate modifications. Preliminary information on this subject was obtained by the oxidation of alpha and beta glucose under such conditions that the interconversion of the alpha and beta isomers is slow in comparison with the oxidation reaction. The sugar was mixed with a solution containing sodium chlorite and acetic acid at 0° C, and the oxidation

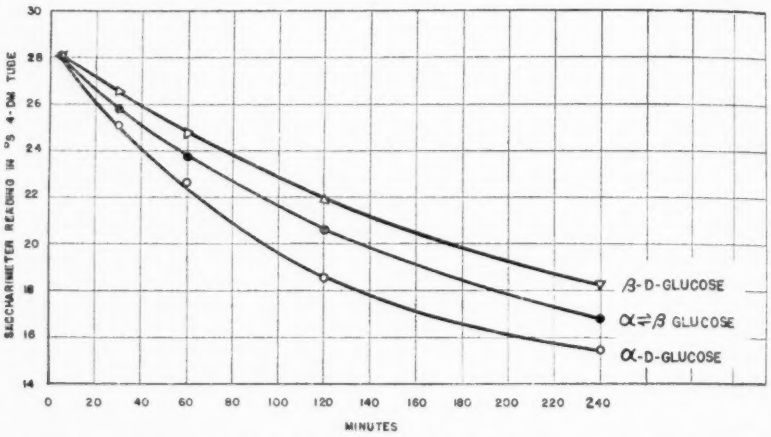

FIGURE 1.— *The oxidation of the alpha and beta modifications of d-glucose by chlorous acid at 0° C.*

The reaction solutions were prepared at 0° C from 0.056 mole of the sugar, 0.167 mole of sodium chlorite, and 0.167 mole of acetic acid in sufficient water to give 100 ml at 0° C. At intervals 12-ml samples were removed and added to equal volumes of 3*M* sodium bisulfite solution at 0° C. The temperature was allowed to rise to 20° C, and after 24 hours the optical rotation of the sample was read in a 4-dm tube.

was followed by optical rotation measurements made on samples of the solution taken from time to time. The oxidation reaction in the samples was stopped by the addition of sodium bisulfite, and the optical rotation of the sample was read after equilibrium was established. The results so obtained are recorded in figure 1.

A comparison of the curves given in figure 1 shows that *α-d*-glucose is oxidized by chlorous acid slightly more rapidly than *β-d*-glucose. The relationship is the opposite of that found by one of us for the oxidation of the *α*- and *β*-aldoses with bromine water [5, 6], in which case it will be recalled that *β-d*-glucose is oxidized approximately 50 times as fast as *α-d*-glucose. As might be expected, the curve obtained for the data representing the oxidation of glucose in the equilibrium solution lies between the curves representing the oxidation of the alpha and beta isomers. A difference in the rates of oxidation for the alpha and beta isomers also explains the small rise in optical rotation observed during the oxidation of xylose (see table 3).

III. EXPERIMENTAL DETAILS

1. REACTIONS OF CARBOHYDRATES WITH CHLORITE SOLUTIONS

In order to obtain information as to which carbohydrate groups are reactive and as to the conditions which are suitable for a more detailed investigation, certain typical sugars and sugar derivatives were treated with chlorites under a variety of conditions and the reactions were followed by determinations of optical rotation and of reducing power, and by titration of the oxidizing agent. The results of these measurements are reported in tables 1, 2, and 3. In the reactions utilizing sodium chlorite, calcium chlorite, and calcium chlorite with calcium carbonate, the sugar or its derivative was dissolved in water and allowed to come to equilibrium, after which 50 ml of the chlorite solution was added and the volume made to 100 ml. The sodium chlorite solution was approximately 1.1 *M*, while the calcium chlorite was about 0.5 *M*. In the reactions in which sodium chlorite was used in conjunction with sodium bicarbonate, the sugar or sugar derivative was dissolved in 25 ml of sodium bicarbonate solution (saturated at 20° C) and allowed to come to equilibrium. Then 50 ml of 1.1 *M* sodium chlorite solution was added and the solution was made to 100 ml by the addition of saturated sodium bicarbonate solution. In the reactions using calcium chlorite in the presence of calcium carbonate, 100 ml of the sugar-calcium chlorite solution was poured into a bottle containing 10 g of precipitated calcium carbonate, which was kept in suspension by frequent shaking. On account of the large amount of gas liberated, the oxidations with chlorous acid were conducted in a slightly different manner and will be described in a subsequent paragraph. The solutions containing the reacting mixtures were kept in a room maintained at 20° C, from which sunlight was excluded. From time to time samples were taken and analyzed in the following manner:

Ten milliliters of the solution undergoing oxidation was transferred to a 2-dm polariscope tube and the optical rotation was read. Then 5 ml of the solution was removed from the polariscope tube and diluted to 25 ml. The solution remaining in the tube was used for the measurement of pH with a conventional pH meter, using a glass electrode. A 10-ml sample of the diluted solution was then slowly added to a solution prepared from 15 ml of 10-percent potassium iodide and 15 ml of 30-percent acetic acid. The iodine liberated was titrated in a 100-ml sugar flask with a 0.2 *N* sodium bisulfite solution [5] standardized at frequent intervals with potassium dichromate solution. The titration is a measure of the quantity of chlorite and chlorine dioxide in the solution [7]. The solution from the sodium bisulfite titration was cooled in ice water and neutralized to phenolphthalein with 30-percent sodium hydroxide solution, and ultimately made up to 100 ml at 20° C. From this neutral solution, samples of 5 or 10 ml were taken for the determination of reducing-sugar values by means of the modified Scales procedure and the factors determined by Isbell, Pigman, and Frush [8].

The measurements utilizing chlorous acid were conducted in sealed tubes using essentially the same proportions of sugar and oxidant as

[5] Sodium thiosulfate could not be employed for this titration because the tetrathionafe formed from sodium thiosulfate interferes in the subsequent determination of reducing sugar.

were employed in the measurements using chlorites. The sugar or sugar derivative and phosphoric acid were placed in the tube, prepared for sealing. After the tube and contents were cooled in ice water, the required quantity (10 ml) of 1 *M* sodium chlorite solution was added and the tube was sealed at once. The tubes were kept for about 15 minutes in cold water and were then placed in a dark room at 20° C and allowed to stand until opened for analysis. A number of tubes were made up for each reaction mixture, and at stated intervals the tubes were opened and the contents were analyzed. Immediately after opening a tube, 5 ml of the solution was removed and diluted to 25 ml for the determination of the oxidant and the reducing sugar by the procedure described in the preceding paragraph. The solution remaining in the tube was used for the determination of optical rotation and pH. Some of the reactions were very rapid, and it was necessary to estimate the constants at zero time by indirect methods. The initial pH values of the highly reactive sugars were postulated to be the same as those given by sucrose under like conditions; the values for the initial optical rotations and the reducing sugars were determined by measurements on samples of the sugar containing phosphoric acid diluted with water, instead of with the sodium chlorite solution. The initial bisulfite titration was estimated by titration of a solution containing sodium chlorite and water diluted as described for the samples containing the sugars.

In the experiments reported in tables 1 to 4 approximately 0.056 mole of the carbohydrate was treated with 0.056 mole of chlorite in 100 ml. This proportion of chlorite is only one-third of that required for the oxidation of the aldoses by reaction V. Experiments using the theoretical quantity of chlorite have shown that the reactions are essentially the same as those in which only one-third the theoretical amount of chlorite was used.

2. ACTION OF CHLORINE DIOXIDE ON SUGARS

Chlorine dioxide was generated in an all-glass apparatus from a mixture of 25 g of potassium chlorate and 20 g of oxalic acid dihydrate, to which 80 ml of a cold solution of sulfuric acid (made from 40 ml of concentrated sulfuric acid and 90 ml of water) was added [3,9]. The mixture was well shaken and then warmed to 58° C in a water bath to initiate reaction and was kept at 50° to 58° C during the reaction. The chlorine dioxide gas was passed through water to wash it before it was absorbed in 250 ml of water kept at 0° C by an ice bath. The reaction was complete in about 1 hour and gave about 8 g of chlorine dioxide in solution.

The measurements recorded in table 5 were conducted in the following manner: Ten-gram samples of glucose, fructose, and sucrose, and an 8.325-g sample of *l*-arabinose were made up to 50 ml with water. Ten milliliters of these solutions were introduced into tubes prepared for sealing, and the tubes and contents cooled to 0° C. Ten milliliters of the previously prepared ice-cold chlorine dioxide solution was then added to each tube while cooling was continued, and the tube was sealed and kept in the dark at 20° C. At stated intervals the solutions were sampled, the optical rotations and the reducing-sugar content were determined, and the sodium bisulfite titration was performed in the manner described for the reactions using chlorous acid.

3. ANALYSIS OF OXIDATION PRODUCTS FOR CHLORIDE, CHLORITE, CHLORATE, AND CHLORINE DIOXIDE

The investigations in which the reactions were followed by the amount of oxidation were supplemented by experiments in which the degradation products of the oxidant were determined. In these experiments, the quantity of chlorite consumed in the reaction was calculated from the difference between the amount added and that remaining in the sample. The latter was determined by titration in acetic acid solution with thiosulfate according to the method described in reference [7]. Before titration the chlorine dioxide was removed by passing nitrogen through the solution. Chloride was determined as silver chloride in the conventional manner, and the "total chlorine content" of the solution after removal of the chlorine dioxide was determined by reducing all the chlorine compounds to chloride by heating with zinc according to the method described on page 408 of reference [10]. The total chlorine content of the solution consists of the chloride, chlorite, and chlorate chlorine, and hence the chlorate chlorine was obtained by subtracting the chloride and chlorite chlorine from the total. The amount of chlorine dioxide was calculated from the difference between the chlorine originally added as chlorite and the chlorine content determined after removing the chlorine dioxide by volatilization. This calculation is based on the assumption that the only volatile product containing chlorine is chlorine dioxide. The results obtained by these methods are given in tables 7 and 10 and are discussed on page 132.

TABLE 10.—*Products formed by the oxidation of d-glucose with chlorites in acid and in neutral solutions*

Constituents	I 0.0555 mole of *d*-glucose+0.1516 mole of $NaClO_2$+0.168 mole of acetic acid in 100 ml at 0° C for 24 hours	II 0.0555 mole of *d*-glucose+0.0531 mole of $NaClO_2$+0.056 mole of acetic acid in 100 ml at 20° C for 24 hours	III 0.0555 mole of *d*-glucose+0.0248 mole of $Ca(ClO_2)_2$ in 100 ml+$\overline{CaCO}$ at 20° C for 7 days
	Moles	*Moles*	*Moles*
Chlorite (initial)	0.1516	0.0531	0.0495
Chlorite unreacted	.0000	.0001	.0081
Chlorous acid consumed	.1516	.0530	.0414
Glucose oxidized	.0396	.0166	.0160
Total chlorine in nonvolatile products	.0721	.0230	.0359
Chloride formed in reaction	.0533	.0206	.0197
Chloride plus chlorate, formed	.0721	.0229	.0278
Chlorate, formed	.0187	.0023	.0081
Chlorine dioxide lost	.0796	.0301	.0136

4. ISOLATION OF THE OXIDATION PRODUCTS

(a) OXIDATION OF *d*-GLUCOSE IN NEUTRAL SOLUTION

Twenty-five grams of *d*-glucose and 12 g of calcium chlorite were dissolved in water and made to a volume of 250 ml. This solution was mixed in a glass-stoppered flask with 25 g of precipitated calcium carbonate and allowed to stand at 20° C in the dark with occasional shaking. In the course of 7 days, the glucose content dropped from 100 mg/ml to 66 mg/ml and the pH changed from 7.2 to 5.9. On the 7th, 9th, and 15th days, 6-g portions of calcium chlorite were added.

On the 16th day the glucose content was 32 mg/ml; at this time the solution was placed in a distillation flask and the chlorine dioxide was removed by volatilization in vacuo at room temperature. The solution containing calcium carbonate and calcium oxalate in suspension was filtered and the insoluble residue washed with hot water.

The calcium carbonate residue was dried, and the amount of calcium oxalate was determined by titration in sulfuric acid solution with potassium permanganate. The titration showed the presence of 0.492 g of calcium oxalate in the residue. This corresponds to 1 molecule of oxalic acid for each 24.6 molecules of glucose oxidized.

The solution, containing the soluble products from the oxidation described above, was added slowly to 50 g of lime in 150 ml of water. The resultant mixture was heated to 50° C, filtered, and the insoluble basic calcium salts were washed with saturated limewater. The basic salts were then suspended in water and treated with carbon dioxide until neutral to phenolphthalein. The carbonated solution was heated to boiling, filtered, and concentrated *in vacuo* to a thin sirup; sufficient alcohol was added to saturate the solution, which was then seeded with calcium gluconate. After 24 hours the product was removed by filtration, washed with 75-percent aqueous alcohol, and air-dried. The crystals weighed 3.5 g and gave $[\alpha]_D^{20}=+8.5$ (water; c,[6] 3). Calcium gluconate has a specific rotation of +8.5 [11]. The mother liquor gave a small second crop of crystalline calcium gluconate, but the residue could not be brought to crystallization.

(b) OXIDATION OF *l*-ARABINOSE IN NEUTRAL SOLUTION

Twenty-one grams of *l*-arabinose and 12 g of calcium chlorite were dissolved in water and the volume was made to 250 ml. The solution was mixed in a glass-stoppered flask with 25 g of precipitated calcium carbonate and allowed to stand at 20° C in the dark with occasional stirring. After 2 days the sugar content had dropped from 83.24 to 44.40 mg/ml and the pH had changed from 7.5 to 5.5. On the 2d and 5th days, 6-gram portions of calcium chlorite were added. On the 6th day, when the sugar content had dropped to 6 mg/ml and considerable calcium arabonate had crystallized from solution, the chlorine dioxide was removed by volatilization at room temperature and the residual calcium salts were collected on a filter and washed with water. The calcium arabonate in the filtrate was separated by precipitation with 50 g of hydrated lime. The basic salt was collected on a filter and washed with limewater. Then the basic salt was suspended in water and carbonated until neutral to phenolphthalein. The mixture was heated to boiling, and the calcium carbonate was removed by filtration and washed with hot water. The filtrate and washings were concentrated *in vacuo* until crystallization began, when 3 volumes of 50-percent aqueous methyl alcohol was added. On standing, 3.4 g of crystalline calcium arabonate separated. The air-dried salt gave $[\alpha]_D^{20}=+2.81$ (water; c, 2.3) and contained 8.66 percent of calcium. Calcium arabonate, $Ca(C_5H_9O_6)_2.5H_2O$, gives $[\alpha]_D^{20}=+2.97$ [12] and has a calcium content of 8.69 percent. The larger part of the calcium arabonate was extracted from the calcium carbonate residue separated from the original reaction mixture. This material was extracted with boiling water and the water solution was evaporated

[6] Throughout this article c designates the concentration of the optically active substance in grams per 100 ml of solution.

and brought to crystallization. The first crystals weighed 3.63 g, gave $[\alpha]_D^{20}=+2.85$ (water; *c*, 2.3), and contained 8.90 percent of calcium. The second crop of crystals weighed 5.84 g, gave $[\alpha]_D^{20}=+3.16$ (water; *c*, 2.3), and contained 8.58 percent of calcium. The total quantity of calcium arabonate separated was 12.88 g. As final proof of the identification of this material, it was converted into crystalline *l*-arabonic acid, which was found to melt at 112° to 114° C in agreement with the recorded value [13].

Part of the insoluble calcium carbonate residue after extraction of the calcium arabonate was dissolved in sulfuric acid and titrated with potassium permanganate. The titration showed a total of 0.767 g of calcium oxalate in the residue. This corresponds to 1 mole of oxalic acid for each 21.6 moles of arabinose oxidized. The identity of the salt was established by the isolation of crystalline oxalic acid from the residue.

(c) OXIDATION OF LACTOSE IN NEUTRAL SOLUTION

Forty-eight grams of anhydrous lactose and 12 g of calcium chlorite were dissolved and made up to 250 ml with water. This solution was mixed with 25 g of precipitated calcium carbonate in a glass-stoppered flask and allowed to stand at 20° C in the dark with occasional shaking. After 2 days the solution was yellow with chlorine dioxide gas. By the 5th day the color of the solution had diminished considerably and 12 g of calcium chlorite was added. Likewise, on the 7th day 12 g of calcium chlorite was added. On the 10th day the chlorine dioxide was removed from the mixture at 20° C *in vacuo* and the solution was filtered. It was found that the reducing sugar had changed from 192 to 70.20 mg/ml, and the pH from 7.5 to 5.4. The unreacted calcium chlorite in the total solution was about 0.5 g. The insoluble residue, which consisted of a mixture of calcium carbonate and calcium oxalate, was extracted with hot water and dried. The calcium oxalate present, determined by permanganate titration in sulfuric acid solution, was 0.124 g. This corresponds to 1 mole of oxalic acid for each 88 moles of lactose oxidized. The filtrate was treated with 50 g of freshly hydrated lime. The resultant mixture was warmed to 50° C, and the insoluble basic salts were removed and washed with saturated limewater. The basic salts, suspended in water, were carbonated until neutral to phenolphthalein. The mixture was heated to boiling and filtered, and 30 g of $CaBr_2\ 6H_20$ (1.1 *M* equivalents) was added. The solution was concentrated *in vacuo* to a thick syrup, and crystallization was initiated by saturating the solution with alcohol and seeding with calcium lactobionate–calcium bromide crystals. After 24 hours at 4° C the crystals were removed, washed with 50-percent aqueous alcohol, and dried at 50° C. Weight, 8.31 g; $[\alpha]_D^{20}=+18.8$ (water; *c*, 7.3). Calcium lactobionate–calcium bromide ($Ca(C_{12}H_{21}O_{12})_2\ CaBr_2{\cdot}6H_2O$) gives $[\alpha]_D^{20}=+18.7$ [14].

IV. REFERENCES

[1] M. C. Taylor, J. F. White, G. P. Vincent, and G. L. Cunningham, Ind. Eng. Chem. **32,** 899 (1940).
[2] J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. II, p. 281 (Longmans, Green and Co., London, 1922).
[3] E. Schmidt and E. Graumann, Ber. deut. chem. Ges. **54,** 1860 (1921).
[4] H. S. Isbell and C. S. Hudson, BS J. Research **8,** 327 (1932) RP418.
[5] H. S. Isbell, BS J. Research **8,** 615 (1932) RP441.

[6] H. S. Isbell and W. W. Pigman, BS J. Research **10,** 337 (1933) RP534; 18, 141 (1937) RP969.
[7] D. T. Jackson and J. L. Parsons, Ind. Eng. Chem., Anal. Ed. **9,** 14 (1937).
[8] H. S. Isbell, W. W. Pigman, and H. L. Frush, J. Research NBS **24,** 241 (1940) RP1282.
[9] E. Schmidt, E. Geisler, P. Arndt, and F. Ihlov, Ber. deut. chem. Ges. **56,** 23 (1923).
[10] F. P. Treadwell and W. T. Hall, Analytical Chemistry, vol. II, p. 408 (John Wiley & Sons, Inc., New York, N. Y., 1935).
[11] C. S. Hudson and H. S. Isbell, BS J. Research **3,** 59 (1929) RP82.
[12] H. S. Isbell, J. Research NBS **14,** 307 (1935) RP770.
[13] H. S. Isbell and H. L. Frusch, BS J. Research **11,** 662 (1933) RP613.
[14] H. S. Isbell, J. Research NBS **17,** 333 (1937) RP914.

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STUDIES OF THE CHEMICAL DURABILITY OF GLASS BY AN INTERFEROMETER METHOD

By Donald Hubbard and Edgar H. Hamilton

ABSTRACT

An interferometer method for determining the chemical durability of glass has been tried on a series of typical glasses over a wide range of temperature and pH. The results emphasize the importance of careful temperature control if comparisons are to be made between the findings of different investigators. The relations between amount of attack and pH for some of the glasses show pronounced inflections near pH 7 in the presence of Britton universal buffer, while the attack by distilled water for these same glasses is very slight in comparison. Moreover, the results strongly emphasize the fact that there can be no single test by which the durability of glass can be judged with respect to all conditions of service.

The method has proved particularly useful in the interpretation of known voltage anomalies of the glass electrode.

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I. INTRODUCTION

Of the many methods proposed for determining the relative "chemical durability" of glasses none has met with universal approval and none is completely fair to all types of glasses [1].[1] The present paper reports the results of direct measurement, by means of an interferometer, of the rates of attack of several types of glass by various reagents over a wide range of conditions of temperature, time, and pH. If durability is defined as the resistance of glass to attack by a specified reagent, the method herein described provides a simple way of determining it in those instances in which the attack is relatively rapid.

Although the interferometer method [2, 3, 4, 5] as thus far used is not highly precise or accurate, it does yield results which appear to give a clearer picture of the durability of glasses over a much wider range of conditions than any of the methods previously proposed.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. EXPERIMENTAL PROCEDURE

The specimens of glass were rectangular, approximately 2 by 3 cm, with surfaces sufficiently flat to show interference bands when placed under a slab of optically flat fused quartz. These specimens were partially immersed approximately one-third of their length in the desired solution, the surface of which was covered throughout the period of the test with a thin layer of liquid petrolatum to prevent evaporation. All the durability tests were made in Pyrex beakers. The desired temperature was maintained within $\pm 0.2°$ C by means of an electrically heated water bath. Uniform attacks upon the immersed surfaces were obtained, except that, under certain conditions, a more pronounced attack occurred just at the oil-solution interface than elsewhere. The resulting indentations are referred to in table 4 as "surface cuts." At the end of the period of the treatment the specimens were removed and rinsed, first in dilute acid and then in water to stop further attack.

The magnitude of the attack, that is the thickness of glass dissolved away, or the thickness added by swelling, was determined by observing the displacement of the interference fringes when the specimen was placed under a fused quartz optical flat. The quartz flat in this case must have both surfaces polished "true plane" and adjusted to make an angle of 20″ with each other, so that the light reflected from the upper surface will not be reflected back to the observer. The observations were made with the conventional Pulfrich viewing apparatus, using an unfiltered helium lamp for illumination. The values were recorded to a quarter of a fringe with a further gradation of + and − to designate that the attack was slightly more or less than the recorded value. Greater precision might be obtained with a micrometer eyepiece. For very small attacks, "detectable" and 1/10 fringe were also used to express the degree of alteration of the surface. If the specimens are viewed with monochromatic light, there is no indication as to the whole number of fringes which should be counted to measure the degree to which the surface has been altered. However, with the filter removed, the color pattern for the fringes in the unattacked portion of the specimen persists in the attacked area, making the total amount of shift readily apparent. Furthermore, without the filter it is easy to determine whether the specimen has swollen or has been dissolved away during the exposure to the solution, by observing the direction of shift of the interference bands. Each band displacement is approximately equivalent to an attack of 0.29 micron. Although in these experiments the determinations were made with the Pulfrich viewing apparatus, equally satisfactory results can be obtained with a simple 25-watt incandescent light mounted in any convenient housing for shielding the eyes from the direct glare. With this illumination and with the aid of a hand magnifying glass for viewing the bands, the observations can be made as conveniently as, or perhaps more conveniently than, with the more expensive Pulfrich apparatus.

III. DURABILITY OF GLASSES UNDER VARIOUS CONDITIONS

1. EFFECT OF DURATION OF EXPOSURE AT CONSTANT TEMPERATURE

In table 1 are listed the attacks in interference bands for five commercial glasses and three optical glasses resulting from treatment with 5-percent NaOH (sodium hydroxide) at 80° C for various time intervals ranging from 15 minutes to 6 hours. These data, as plotted in figure 1, indicate that the reduction in thickness of each glass was directly proportional to the duration of treatment. The rates of attack for the different glasses, listed as a in column 2 of table 3, could

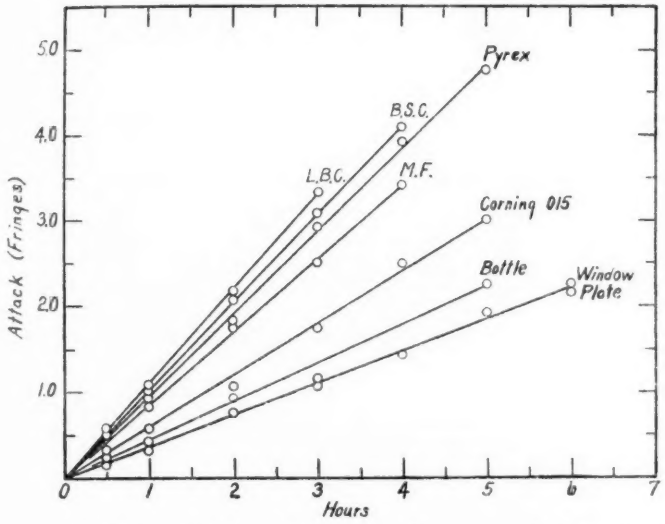

FIGURE 1.—*Attack-time plot for eight types of glasses exposed to 5-percent* NaOH *at 80° C.*

be used to represent the relative order of durability of these glasses with respect to this solution at the specified temperature. However, since the chemical durability of the glasses decreases with increasing slopes, it is perhaps desirable to take the reciprocals of these values in order that the glasses with the better chemical durabilities may be represented by the larger numerical values. The chemical durability of glass under these conditions could thus be defined as the time required for one unit (fringe) change of thickness, or

$$\text{Chemical durability} = 1/a, \text{ where } a = \frac{\text{attack in fringes}}{\text{time in hours}}.$$

Values of $1/a$ are given in column 3 of table 3.

TABLE 1.—*Attack in terms of interference bands by 5-percent* NaOH *at 80° C on eight types of glass*

Time	Plate	Window	Am. Cer. Soc. bottle No. 1	Corning 015	M. F.[1]	Chemical Pyrex	B. S. C.[1]	L. B. C.[1]
	Fringes	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
15 minutes	$<\frac{1}{10}$				$\frac{1}{4}-$		$\frac{1}{4}$	$\frac{1}{4}+$
30 minutes	$>\frac{1}{10}$			$\frac{1}{4}$	$\frac{1}{4}+$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}+$
1 hour	$\frac{1}{4}+$	$\frac{1}{4}+$	$\frac{1}{2}-$	$\frac{1}{2}+$	$\frac{3}{4}+$	1−	1	1+
2 hours	$\frac{3}{4}$	$\frac{3}{4}$	1−	1+	$1\frac{1}{4}$	$1\frac{3}{4}+$	2+	$2\frac{1}{4}-$
3 hours	1+	$1\frac{1}{4}-$		$1\frac{3}{4}$	$2\frac{1}{2}$	3−	3+	$3\frac{1}{4}-$
4 hours	$1\frac{1}{2}-$	$1\frac{1}{2}-$		$2\frac{1}{2}$	$3\frac{1}{2}-$	4−	4+	
5 hours	2−	2−	$2\frac{1}{4}$	3		$4\frac{3}{4}$		
6 hours	$2\frac{1}{4}-$	$2\frac{1}{4}$						

[1] M. F.; B. S. C.; and L. B. C. are optical glasses: medium flint, borosilicate crown, and light barium crown, respectively.

TABLE 2.—*Attack in interference bands by 5-percent* NaOH *for 3 hours at various temperatures*

Temperature °C	Plate	Window	Am. Cer. Soc. bottle No. 1	Corning 015	M. F.[1]	Chemical Pyrex	B. S. C.[1]	L. B. C.[1]
	Fringes	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
30					D[2]		D	$\frac{1}{10}-$
40	$\frac{1}{10}-$	D	D	D	$\frac{1}{10}$	$\frac{1}{10}$	$\frac{1}{10}+$	$\frac{1}{10}$
50	$\frac{1}{10}+$	$\frac{1}{10}+$	$\frac{1}{10}+$	$\frac{1}{10}+$	$\frac{1}{4}-?$	$\frac{1}{4}$	$\frac{1}{4}+$	$\frac{1}{2}-$
60	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}+$	$\frac{1}{4}+$	$\frac{1}{2}+$	$\frac{1}{2}+$	$\frac{3}{4}$	$\frac{3}{4}+$
70	$\frac{1}{2}+$	$\frac{1}{2}+$	$\frac{3}{4}$	1−[3]	$1\frac{1}{4}$	$1\frac{1}{2}-$	$1\frac{1}{4}$?	$1\frac{1}{4}-$
80	1+	$1\frac{1}{4}-$	$1\frac{1}{2}-$	$1\frac{3}{4}$	$2\frac{1}{2}$	3−	3+	$3\frac{1}{4}$
90	2+	2+	3−	>3, <4		>5, <6		

[1] M. F.; B. S. C.; and L. B. C. are optical glasses: medium flint, borosilicate crown, and light barium crown, respectively.
[2] D, detectable.
[3] Poor cut.

TABLE 3.—*Values of the constants a and b from the data in table 1 and table 2 for 5-percent* NaOH *solution*

[(1) Attack at 80° C = $a \times$ hours; (2) Attack/hours = $b \times (2)^{t/10}$]

Glass	a	$1/a$	b[1]
	Fringes/hour	*Hours/fringe*	*Fringes/hour*
Plate	0.37	2.70	0.0014
Window	.37	2.70	.0014
Am. Cer. Soc. Bottle No. 1	.47	2.13	.0018
Corning 015	.59	1.69	.0023
M. F.[2]	.83	1.20	.0033
Chemical Pyrex	.95	1.05	.0037
B. S. C.[2]	1.02	0.98	.0040
L. B. C.[2]	1.10	.91	.0043

[1] Inspection of the constant b shows it to be the attack in fringes (extrapolated to 0° C) for 1 hour's exposure to 5-percent NaOH solution. Hence an intercomparison of the constants a and b can be had by the simple relation $a = b \times (2)^{80/10}$.
[2] M. F.; B. S. C.; and L. B. C. are optical glasses: medium flint, borosilicate crown, and light barium crown, respectively.

2. EFFECT OF TEMPERATURE FOR CONSTANT PERIODS OF EXPOSURE

The attack of glass by aqueous solutions as ordinarily observed has to do with a rate of reaction; hence the term "solubility", which means strictly the quantity of a substance which will dissolve in a given quantity of a solvent at a specified temperature, when equilibrium is attained, should not be used in this connection. Further-

more, the reaction whose rate as observed is not necessarily a process of solution only, but it may involve solution of some constituent, followed by mechanical removal of individual products of decomposition from the affected area. It cannot be too strongly emphasized that this type of reaction is highly sensitive to slight differences in experimental conditions, such as pH and temperature [1, 4]. Figure 2, plotted from the data in table 2, shows graphically the effect of increasing temperature upon the amount of glass removed by chemical attack during a 3-hour interval in which the same glasses as those reported in figure 1 were exposed to 5-percent NaOH. Within

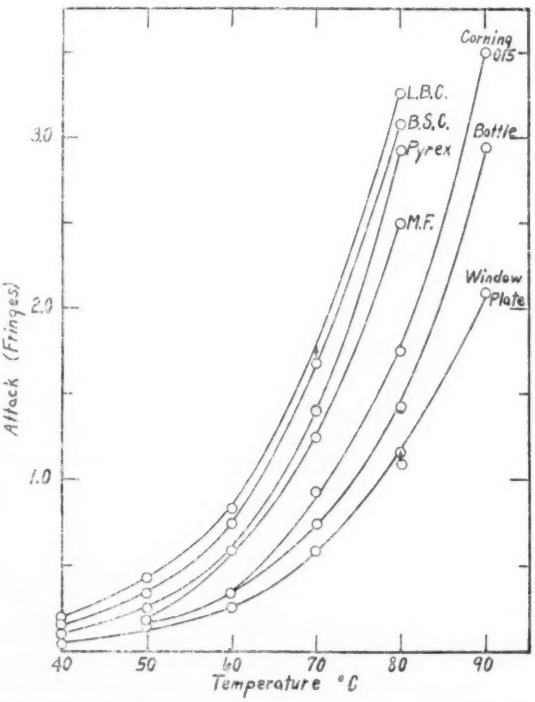

FIGURE 2.—*Temperature effects on rate of attack for eight types of glasses in 5-percent* NaOH *for 3 hours.*

reasonable limits the attack follows the usual approximation that the rate of reaction doubles for each 10° C rise in temperature, which relation may be expressed in the equation

$$\text{Attack/hours} = b \times (2)^{t/10}, \tag{1}$$

where b is a constant and t is temperature in degrees centigrade. This relation must not be considered rigorously accurate, but it does emphasize the importance of very careful temperature control. Values of b which are listed in column 4 of table 3 could be used as an index of relative durability for these glasses in 5-percent NaOH.

A classical relation is that proposed by Arrhenius [6] and given in the following equation:

$$\frac{d\ln k}{dT}=\frac{E}{RT^2}, \tag{2}$$

in which k is the reaction rate or, in this case, attack on the glass in fringes per unit of time, E is a constant, R is the gas constant, and T is the absolute temperature. Integrating eq 2, we have

$$\log k=-\frac{E}{2.303RT}+C=-\frac{B}{T}+C, \tag{3}$$

where $B=(E/2.303R)$ and C is a constant. Geffcken and Berger [5] found this relation to apply to the attack of Na_2CO_3 solutions on a borosilicate crown glass. Müller and Weinstein [7] found that it

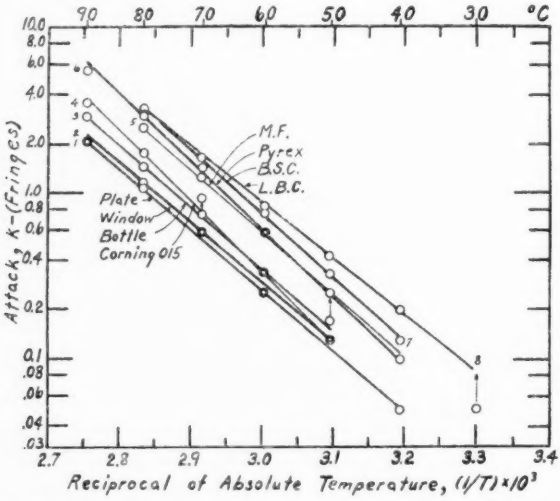

FIGURE 3.—*Log attack, k, versus reciprocal absolute temperature, 1/T.*

Cases in which values coincide for different glasses are indicated by heavy walled circles. Temperature in °C inserted for convenience.

1. Plate glass.
2. Sheet glass.
3. American Ceramic Society bottle No. 1.
4. Corning 015 glass.
5. Medium flint glass.
6. Pyrex.
7. Borosilicate crown.
8. Light barium crown.

applies to the attack of water on borosilicate glasses when the amount of B_2O_3 in the glass is greater than 0.1 percent. Hamilton and Hubbard [8] found that it is also applicable to the attack of water on a number of bottle glasses.

In figure 3 the attack by 5-percent NaOH solution in 3 hours on the eight different glasses of table 1 are plotted *on a log scale* against the reciprocal of the absolute temperature. For each glass these points

plot as a straight line within the limit of error in determining the amount of attack. The equations for these lines are

Plate glass	$\log k = -\frac{3600}{T} + 10.23$
Window glass	$= -\frac{3600}{T} + 10.26$
Am. Ceram. Soc. Bottle No. 1	$= -\frac{3960}{T} + 11.38$
Corning 015 (glass electrode) glass	$= -\frac{4280}{T} + 12.37$
Medium flint (optical) glass	$= -\frac{3870}{T} + 11.37$
Pyrex	$= -\frac{4020}{T} + 11.84$
Borosilicate crown (optical) glass	$= -\frac{3700}{T} + 10.97$
Light barium crown (optical) glass	$= -\frac{3320}{T} + 9.90$

In figure 3 some of the lines cross and, with the possible exception of two lines, the slopes of the individual lines are different. These conditions suggest that it may not be safe to use observations made at high temperatures as criteria of chemical durability at room temperature. The order of relative chemical durability of a series of glasses at elevated temperatures may not be the same as at room temperature. Taylor and Smith [9] in their investigation of the chemical durability of various glasses by the powder method found such reversals. On this basis it would seem advisable when water or alkaline solutions are used as the attacking media to make tests at two or more temperatures and then extrapolate the results to room temperatures by the use of graphs such as those in figure 3.

3. DURABILITY AT DIFFERENT pH VALUES

Of special interest is the variation in the chemical durability of glass over a wide pH range, from acid to highly alkaline solutions. To obtain information on this property, the eight glasses previously described were exposed for 6 hours at 80° C to Britton universal buffer solutions [10] having a pH range from 1.8 to 12. This range was extended to pH 0.65 with a sodium acetate-hydrochloric acid buffer. The results show an interesting variety in the durability of these glasses (table 4). Three of them show no detectable attack after 6 hours at 80° C up to pH 7, beyond which there is a detectable attack at pH 8 and 9, while with further increase in alkalinity the attack increases rapidly. These three glasses are, respectively, American Ceramic Society bottle glass No. 1 [11], a window glass,

and Pyrex. The results for these three glasses, which are plotted in figure 4, are typical of many of the commercial silicate glasses. Pyrex is the least resistant of the three at pH 11 and 12 [12, 1] and this difference becomes more pronounced in the high alkalinity of 5 percent NaOH (figs. 1 and 2).

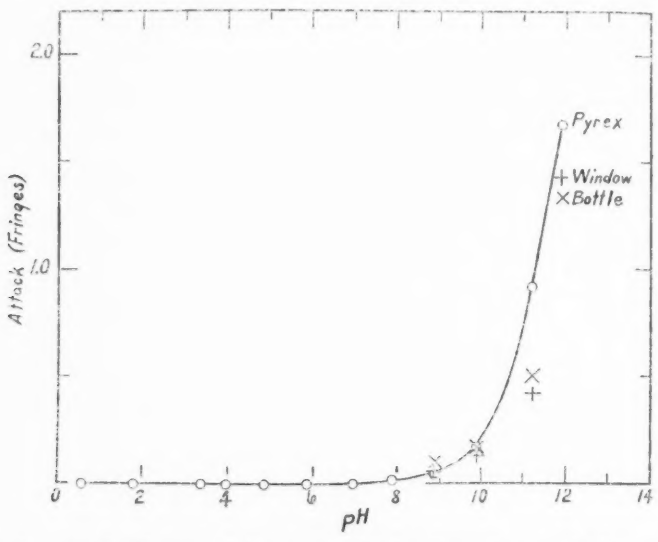

FIGURE 4.—*Attack-*pH *curve 6 hours at 80°C for three glasses which gave no detectable attack in the acid range from* pH *0.65 to 7.*

Beyond pH 8 the glasses are identified by Bottle (×), Window (+), Pyrex (○).

TABLE 4.—*Attack values obtained on eight types of glasses exposed for 6 hours at 80° C to Britton universal buffer covering* pH *range from 1.8 to 11.9*

pH	Plate	Window	Am. Cer. Soc. bottle No. 1	Corning 015	M. F.[3]	Chemical Pyrex	B. S. C.[3]	L. B. C.[3]
	Fringes	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
0.65	ND[1]	ND	ND		ND	ND	¼−	¾
1.8	ND	ND		⅖−, swelling	D[2]	ND	1/10	1/10
3.4		ND		⅖−, swelling	D	ND	D	D
4.0	ND	ND	ND	⅖−, swelling		ND		
4.9	ND	ND		⅖−, swelling	1/10	ND	D	¼−
5.9	D	ND		⅖−, swelling		ND	1/10+	¾
7.0	>for pH 5.9.	ND	ND	D, slight surface cut	1−	ND	¼−	2+, <3
7.9	D			D, surface cut ⅗−	¾	D	¼+	1+
8.9	D	1/10−	1/10	1/10−, surface cut ½−	¼−	D+	½−	¾
9.9	¼−	1/10+	¼−	¼+	¼−	¼−	¾	1−
11.2	1−	½−	½	1−	½−	1−	1¼−	1
11.9	1¾−	1½−	1¼+	1¾, 2−	1−	1¾−	1¾	1¼+

[1] ND, not detectable.
[2] D, detectable.
[3] M. F.; B. S. C.; and L. B. C. are optical glasses: medium flint, borosilicate crown, and light barium crown, respectively.

The plate glass is detectably attacked in the vicinity of neutrality with a noticeable improvement in durability at pH 9, after which the rate of attack increases rapidly with further increase in alkalinity (fig. 5). This durability weakness near neutrality is of interest since

the same thing is shown to a most pronounced degree by the three optical glasses tested (fig. 5).

It should be pointed out also that the chemical durability of a glass to any one reagent cannot be taken as a reliable indicator of its durability to another. For example, the attack on these three optical glasses by the universal buffer in the vicinity of neutrality is very large compared with the attack by distilled water. The latter even after 24 hours at 80° C shows an attack of less than $\frac{1}{10}$ fringe.

Another commercial glass, Corning 015 [13], which has been used so successfully for glass electrodes, exhibits a slight uniform swelling between pH 2 and 7, followed by the pronounced attack character-

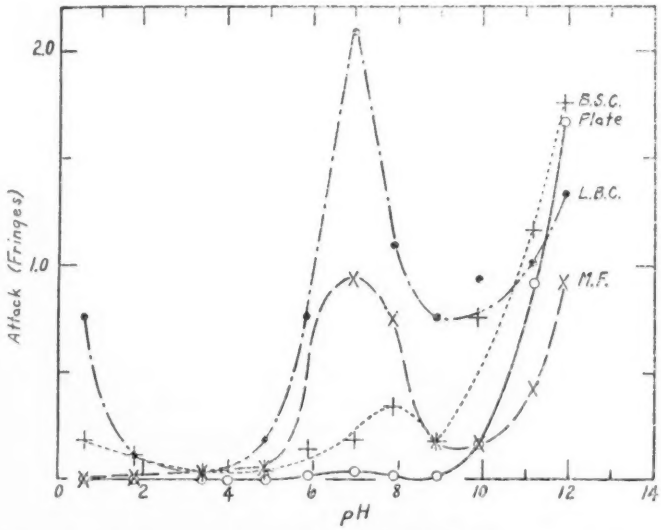

FIGURE 5.—*Attack*-pH *curves for a plate glass* (○) *and three optical glasses, borosilicate crown* (+), *medium flint* (×), *and light barium crown* (•), *showing marked attacks in the region of neutrality after 6 hours' exposure at 80° C.*

istic of silicate glasses at alkalinities above pH 9 (table 4, fig. 6), while in the "super acid" region the swelling is repressed with increasing acid concentration [4] (see fig. 7). The durability characteristics of this glass are particularly interesting, (a) because of the correspondence which the regions of durability change bear to regions of established voltage departures of the glass electrode [13, 4], (b) because this glass is unique among the types investigated, and (c) because of the implications from the pronounced swelling in the acid region. This swelling is probably caused by a preferential solution of certain constituents of the glass, with the resulting glass surface becoming increasingly rich in silica content.

Jones and Homer [16] have found this enrichment in silica content of the surface of optical glasses in the acid region and have found that the resulting surface layer, when of the proper thickness, reduces the reflection of light from this surface, thereby increasing the light transmission of an optical element. The durability curves for the boro-

silicate and light barium crown glasses (fig. 5) show that a minimum loss of thickness occurs near pH 3. From this and other considerations one would expect this region to be an optimum for producing silica-rich surfaces.

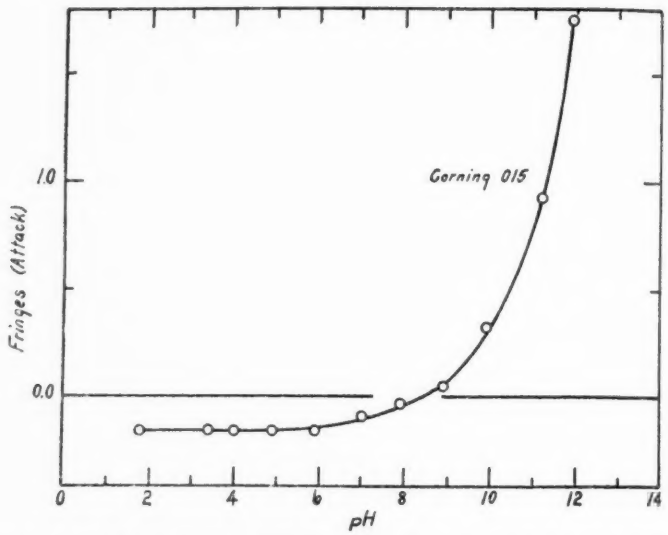

FIGURE 6.—*Attack-*pH *curve for Corning 015 glass, exposed 6 hours at 80° C to Britton universal buffer mixtures covering the range* pH *2 to 12.*

Region of swelling is plotted as negative attack. Reproduced from figure 1, RP1187.

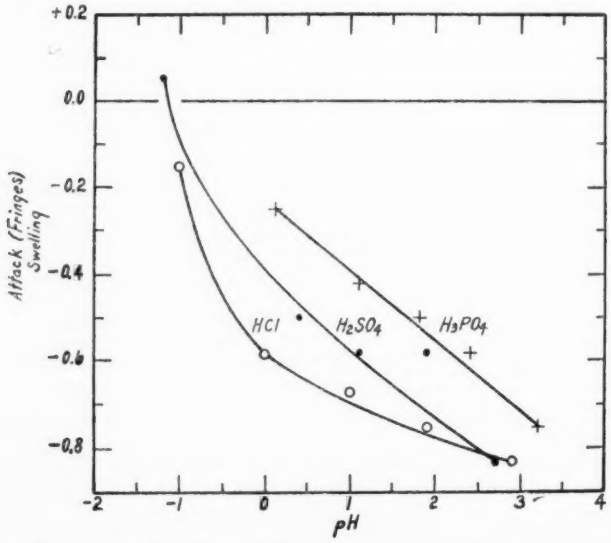

FIGURE 7.—*Repression of swelling of Corning 015 glass by increasing concentrations of* HCl (○), H_2SO_4 (•), *and* H_3PO_4 (+), *for 48 hours at 80° C.*

Reproduced from figure 4, RP1187.

For the Corning 015 glass, attack by distilled water and by the universal buffer near neutrality both cause a small but appreciable swelling. This qualitative agreement of the effect of these two reagents on 015 glass is in extreme contrast to their respective action on the optical glasses.

4. EFFECT OF INCREASED SODIUM-ION CONCENTRATION ON CHEMICAL DURABILITY

The voltage departure of the glass electrode in the alkaline region is increased at any fixed pH and temperature by increasing the sodium-ion concentration [13]. In the light of previous experiments

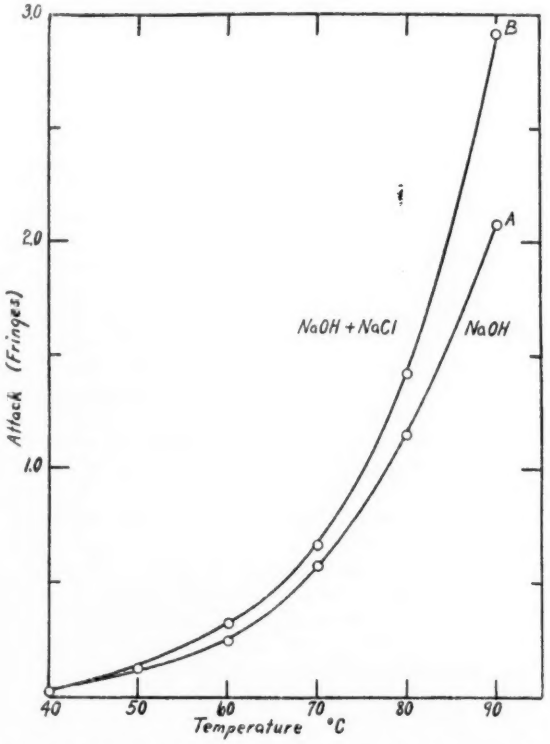

FIGURE 8.—*Attack observed after 3 hours' exposure to 5-percent* NaOH *solution, A; and 5-percent* NaOH *plus an equivalent amount of* NaCl, *B.*

made on voltage departures and durability of the electrode glass [4], it was logical to conclude that additional attack occurs in the presence of increased sodium-ion concentration. To test the validity of this conclusion, samples of an electrode glass were subjected to the action of 5-percent NaOH held at various temperatures for 3 hours; other samples of the same glass were similarly treated with 5-percent NaOH to which an equivalent quantity of NaCl had been added. The results of these two series are given in table 5 and plotted as curves *A* and *B*, respectively, in figure 8. The additional attack

caused by the increased sodium-ion concentration is in qualitative accord with that expected from the voltage departures of the glass electrode.

TABLE 5.—*Attacks obtained on a commercial glass from which successful electrodes were made, after 3 hours' exposure to 5-percent* NaOH, *and 5-percent* NaOH *plus an equivalent amount of* NaCl

Temperature	5-percent NaOH	5-percent NaOH plus equivalent NaCl
°C	*Fringes*	*Fringes*
40	D [1]	D [1]
50	1/10+	1/10+
60	1/4	1/4+
70	1/2+	3/4−
80	1 1/4−	1 1/2−
90	2+	3−

[1] D, detectable.

5. COMPARISON WITH RESULTS OBTAINED BY ANOTHER METHOD

Durability tests of a number of chemical-ware glasses have been made by Wichers, Finn, and Clabaugh [15]. Their method involved determination of the loss in weight of 250-ml Erlenmeyer flasks whose inner surfaces had been subjected to the boiling reagent for a given time. In order to determine whether or not their results agree with those obtained by the interferometer method, comparative tests were made on four commercial glasses used in the manufacture of chemical ware, which were exposed to 0.05*N* and 0.5*N* NaOH for 3 and 6 hours at 80° C. Wichers, Finn, and Clabaugh tested three of these glasses with the same solutions. The data obtained by the interferometer method are recorded in table 6 and plotted in figure 9. The order of decreasing durability found for 0.5*N* NaOH agrees with that determined by Wichers, Finn, and Clabaugh and was as follows: Kimble N–51–a, Tamworth (new Glasbake), Pyrex and Tamworth (old).[2] However, the interferometer method was not sufficiently sensitive to detect attack on any of the four glasses exposed 24 hours at 80° C to *N* H_2SO_4, 5-percent NaCl solution, or distilled water (table 6), while Wichers, Finn, and Clabaugh were able to detect very small durability differences for these different makes of glassware to these solutions. The greater sensitivity of their method can be attributed largely to two factors: (1) the large surface which they used and (2) the elevated temperature. With a temperature of slightly over 100° C, their attack per unit area should be approximately four times that for the 80° C used in the interferometer method.

Prolonged exposures of these four glasses and one bottle glass to *N* H_2SO_4, 5-percent NaCl, and distilled water at 80° C gave the results listed in table 6. A very interesting feature of the acid attack for 7 days at 80° C is that the samples of Pyrex and Tamworth tested showed less resistance to *N* H_2SO_4 than did the American Ceramic Society Bottle Glass No. 1 [11]. Such results should be given further attention. They indicate that the borosilicate laboratory glasswares

[2] The terms "old" and "new" are used to distinguish between a Tamworth glass previously marketed and the product whose analysis is given in the publication by Wichers, Finn, and Clabaugh [15].

possibly do not possess the superior acid resistance that has been accredited to them in the past. The only alternate interpretation of the results is the possibility that the bottle glass may have yielded data which were more favorable than its actual chemical resistance. This could conceivably have occurred through a simultaneous solution and swelling at rates which just counterbalanced each other, but the probability of such a coincidence seems slight.

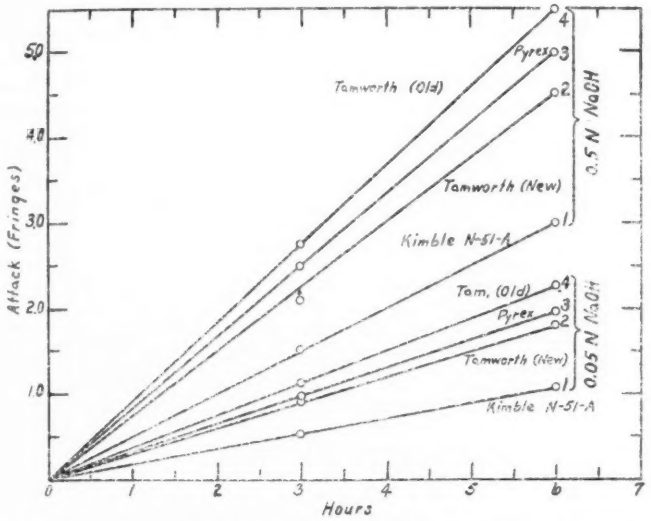

FIGURE 9.—*Comparison of the durability of four glasses used in the manufacture of chemical glassware, to 0.05N and 0.5N* NaOH *at 80° C.*

1. Kimble N-51-A.
2. Tamworth (New).
3. Pyrex.
4. Tamworth (Old).

TABLE 6.—*Durability measurements made at 80° C on four glasses used in the manufacture of chemical laboratory glass and one bottle glass*

Reagent	Exposure time	Attack				
		Kimble N-51-a	Tamworth (new)	Chemical Pyrex	Tamworth (old)	Am. Cer. Soc. Bottle Glass No. 1
	Hours	*Fringes*	*Fringes*	*Fringes*	*Fringes*	*Fringes*
0.05*N* NaOH	3	½+	1−	1	1+	
Do	6	1+	1¼+	2−	2¼	
0.5*N* NaOH	3	1½	2+	2½	2¾	
Do	6	3	4½	5	5½	
N H_2SO_4	24	ND [1]	ND	ND	ND	
Do	168		1/10−	1/10−		ND
Do	336	1/10	1/10+	1/10+	½−	
5-percent NaCl	24	ND	ND	ND	ND	
Do	168		ND	ND		
Do	336	ND	D [2]	D	ND	
Distilled H_2O	24	ND	ND	ND	ND	
Do	336	ND	ND	ND	ND	

[1] ND, not detectable.
[2] D, detectable.

6. COMPARISON OF DURABILITY IN THE PRESENCE OF SODIUM AND POTASSIUM HYDROXIDES

An oral report that burettes were more strongly attacked by aqueous KOH than by NaOH led to a preliminary investigation of the durability of these same four chemical-ware glasses to 0.1 *N* and 1.0 *N* solutions of these hydroxides. The solutions were prepared from freshly opened bottles of NaOH and KOH and standardized against potassium acid phthalate without attempting to remove CO_2. The results obtained are recorded in table 7, and in every case show appreciably more attack by sodium hydroxide than by potassium hydroxide of equal normality. These results are in accord with the generally recognized behavior of these hydroxides [1, p. 132], and are also in agreement with predictions [4 p. 342] based on voltage departures of the glass electrode caused by equal concentrations of Na^+ and K^+ ions [14]. For convenience in visualizing the difference in magnitude between the attack by NaOH and KOH, the data for the more resistant of these glasses, Kimble N–51–A are plotted in figure 10.

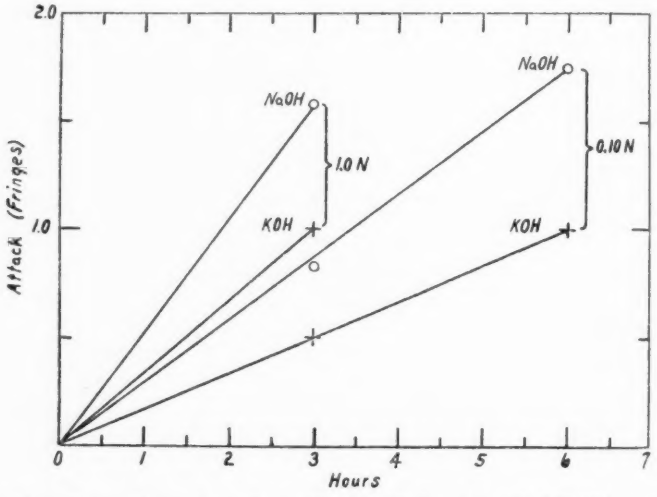

FIGURE 10.—*Comparison of attacks on Kimble N–51–A by* NaOH (○) *and* KOH (+) *of equal concentrations.*

These differences are characteristic of all the four chemical-ware glasses tested.

TABLE 7.—*Comparison of the durability of four chemical-ware glasses to sodium and potassium hydroxides at 80° C*

Reagent	Exposure time	Attack			
		Chemical Pyrex	Kimble N–51–a	Tamworth (old)	Tamworth (new)
	Hours	*Fringes*	*Fringes*	*Fringes*	*Fringes*
N NaOH	3	2½	1½+	2¾+	2¼
N KOH	3	1½+	1	2−	1½+
0.10 *N* NaOH	3	1¼+	¾+	1½	1¼−
0.10 *N* KOH	3	1+	½	1¼−	1+
0.10 *N* NaOH	6	2¾	1¾	3	2¼
0.10 *N* KOH	6	2+	1	2¼	2

IV. SUMMARY

The interferometer method for determining the chemical durability of glass has been applied over an extended range of conditions to a wide variety of glasses. The results obtained show that it is capable of giving useful data under conditions in which the more conventional methods are not applicable.

The authors are indebted to A. N. Finn for his helpful suggestions during the progress of this investigation.

V. REFERENCES

[1] George W. Morey, The properties of glass, American Chemical Society Monograph No. 77, p. 103–134. (Reinhold Publishing Corporation, 330 West 42d St., New York, N. Y., 1938.)
[2] *Relative durability of optical glass.* Tech. News Bul. NBS **221,** 88 (Sept. 1935).
[3] E. Berger, *Grundsätzliches über die chemische Angreifbarkeit von Gläsern I,* Glastech. Ber. **14,** 351 (1936).
[4] Donald Hubbard, Edgar H. Hamilton, and Alfred N. Finn, *Effect of the solubility of glass on the behavior of the glass electrode,* J. Research NBS **22,** 339–349 (1939) RP1187.
[5] V. W. Geffcken and E. Berger, *Grundsätzliches über die chemische Angreifbarkeit von Gläsern II,* Glastechn. Ber. **16,** 296–304 (1938).
[6] F. H. Getman and F. Daniels, Outline of theoretical chemistry, 5th ed., p. 336 (John Wiley and Sons, Inc., New York, N. Y., 1931).
[7] R. L. Müller and C. V. Weinstein, *Untersuchung der Lösungsgeschwindigkeit von Alkaliborgläsern,* Acta Physicochem. U. R. S. S. **3,** 465–502 (1935).
[8] Edgar H. Hamilton and Donald Hubbard, Titration and conductivity measurements of aqueous extracts from bottles (work not yet published).
[9] W. C. Taylor and R. D. Smith, *Solubility characteristics of glasses basically different in composition.* J. Am. Ceram. Soc. **19,** 331 (1936).
[10] T. S. Britton, Hydrogen ions, 2d ed., table 57 (c), p. 225 (D. Van Nostrand and Co., Inc., New York, N. Y. (1932).
[11] Report of Committee on the Chemical Durability of Glass, Bul. Am. Ceram. Soc. **14,** 181 (1935).
[12] P. H. Walker and F. W. Smither, *Comparative tests of chemical glassware,* J. Ind. Eng. Chem. **9,** 1090–1092 (1917).
[13] D. G. MacInnes and M. Dole, *The behavior of glass electrodes of different compositions,* J. Am. Chem. Soc. **52,** 29–36 (1930).
[14] D. G. MacInnes and D. Belcher, *Further studies on the glass electrode,* J. Am. Chem. Soc. **53,** 3315–3331 (1931).
[15] Edward Wichers, A. N. Finn, and W. Stanley Clabaugh, *Comparative tests of chemical glassware,* J. Research NBS **26,** 537 (1941) RP1394.
[16] Frank L. Jones and Howard J. Homer, *Chemical methods for increasing the transparency of glass surfaces,* J. Opt. Soc. Am. **31,** 34–37 (1941).

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EFFECT OF GRAIN SIZE AND HEAT TREATMENT UPON IMPACT-TOUGHNESS AT LOW TEMPERATURES OF MEDIUM CARBON FORGING STEEL

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ABSTRACT

A study was made of the effect of grain size and heat treatment upon the impact-toughness of SAE 1050 steel, as judged by the temperature range wherein cold-brittleness occurred. There was no relation between grain size and impact-toughness in the hot-rolled steels. Normalizing improved this property, and in this condition the fine-grained steels proved superior to the coarse-grained steels. The toughness of the steels, either as hot-rolled or as normalized, was relatively low, but was markedly increased by hardening and tempering. Normalizing prior to heat treatment had no effect upon the impact properties. When heat-treated, there was no relation between grain size and impact-toughness. Each individual heat of steel appeared to have an inherent resistance to impact, dependent upon factors not at present recognized. Impact-toughness at room temperature was no criterion of impact-toughness at lower temperatures.

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I. INTRODUCTION

The purpose of this study was to determine the influence of grain size and heat treatment upon the impact properties at low temperatures of medium-carbon forging steels and to determine the temperature range in which brittleness of the steel occurs. This range is characterized by a marked decrease in the observed impact values accompanied by a change in the appearance of fracture from a fibrous one to a granular one. The study was made in cooperation with the Bureau of Aeronautics, Navy Department.

The technical literature contains numerous references on the impact-toughness of steel. Most data presented appear to substantiate the conclusion that fine-grained steel is superior in toughness to coarse-grained steel [1 to 6],[1] although a contrary opinion has been expressed [7].

II. MATERIALS AND METHODS OF TEST

Six heats of SAE 1050 steel, furnished by the Bethlehem Steel Corporation in the form of hot-rolled 1-in. diameter rods, were used in this study. The chemical compositions of these steels, as deter-

[1] Figures in brackets refer to the literature references at the end of this paper.

mined at this Bureau, are given in table 1. The microstructures and grain sizes of the steels in the as-received condition are shown in figure 1.

Steels *A*, *B*, and *C* were submitted by the manufacturer as having a coarse McQuaid-Ehn grain size and steels *D*, *E*, and *F* a fine grain size. However, tests made by carburizing at 1,700° F for 18 hours (the usual procedure for McQuaid-Ehn tests) showed that steel *C* was a medium fine-grained steel. The grain sizes developed in the McQuaid-Ehn tests are shown in figure 2 and table 2.

Each steel was tested in eight conditions of heat treatment, and the hardness for each was determined (table 3).

TABLE 1.—*Chemical composition of the steels* [1]

Steel	Constituent									
	C	Mn	P	S	Si	O_2	N_2	H_2	Al	Al_2O_3
	%	%	%	%	%	%	%	%	%	%
A	0.49	0.79	0.023	0.023	0.22	0.005 .004	0.004 .005	0.0003 .0001	0.002	0.001
B	.45	.80	.019	.023	.19	.006 .006	.004 .004	.0001 .0001	.002	.001
C	.52	.85	.021	.031	.29	.004 .005	.005 ND [2]	.0002 ND [2]	.002	.005
D	.49	.80	.022	.028	.21	.003 .003	.003 .004	ND [2] .0003	.016	.007
E	.46	.55	.040	.039	.20	.005 .003	.006 .005	.0003 .0003	.019	.004
F	.45	.59	.021	.028	.24	.002 .003	.003 .004	.0002 .0002	.013	.004

[1] Chemical analyses were made by W. H. Jukkola, gas analyses by V. C. F. Holm, both of the National Bureau of Standards.
[2] ND=not detected.

TABLE 2.—*Austenitic grain size of the steels*

Steel	At 1,475° F		At 1,600 F		As hot-rolled		As carburized (McQuaid-Ehn)	
	Grains per sq in. at ×100	ASTM grain size No.	Grains per sq in. at ×100	ASTM grain size No.	Grains per sq in. at ×100	ASTM grain size No.	Grains per sq in. at ×100	ASTM grain size No.
A	50	7	19	5	7	4	35	3
B	50	7	9	4	9	4	35	3
C	110	8	95	7	8	4	37	6
D	150	8	140	8	14	5	100	8
E	150	8	130	8	16	5	110	8
F	130	8	110	8	17	5	105	8

TABLE 3.—*Heat treatment and hardness of the steels*

Heat treatment [a]	Rockwell Hardness number for steels—					
	A	*B*	*C*	*D*	*E*	*F*
As received (hot-rolled)	B 95	B 91	B 97	B 94	B 88	B 89
As received, water-quenched from 1,475° F, tempered at 1,000° F	C 32	C 30	C 33	C 32	C 28	C 29
As received, water-quenched from 1,475° F, tempered at 1,150° F	C 23	C 21	C 24	C 22	C 19	C 19
As received, water-quenched from 1,475° F, tempered at 1,300° F	C 14	C 12	C 14	C 15	C 11	C 11
As normalized (air-cooled from 1,600° F)	B 97	B 93	B 96	B 93	B 89	B 88
Normalized, water-quenched from 1,475° F, tempered at 1,000° F	C 32	C 29	C 32	C 31	C 28	C 28
Normalized, water-quenched from 1,475° F, tempered at 1,150° F	C 22	C 20	C 23	C 22	C 20	C 18
Normalized, water-quenched from 1,475° F, tempered at 1,300° F	C 13	C 13	C 15	C 14	C 11	C 11

[a] All steels were held for 1 hour at normalizing and tempering temperatures and ½ hour at hardening temperatures. Bars were shaped to ½-in. square and cut to lengths of about 15 in. prior to heat treatment.

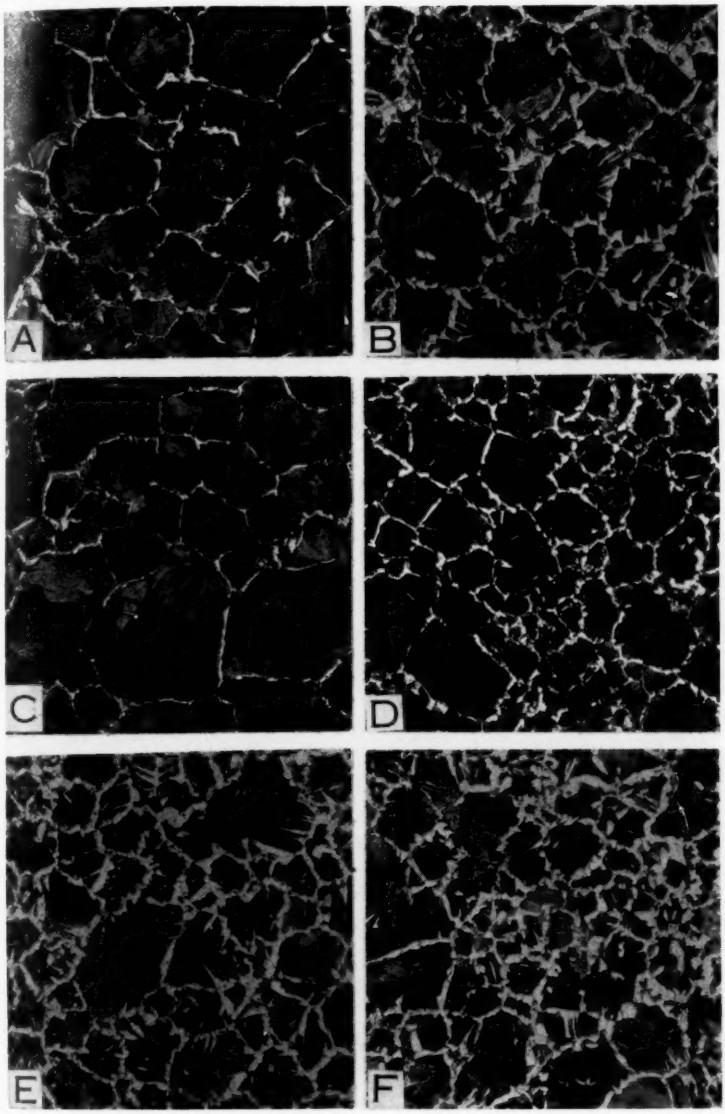

FIGURE 1.—*Microstructures of the steels as hot-rolled.*

Etched with 1-percent nital. ×100. The letters on the micrographs correspond with the designations used for the individual steels.

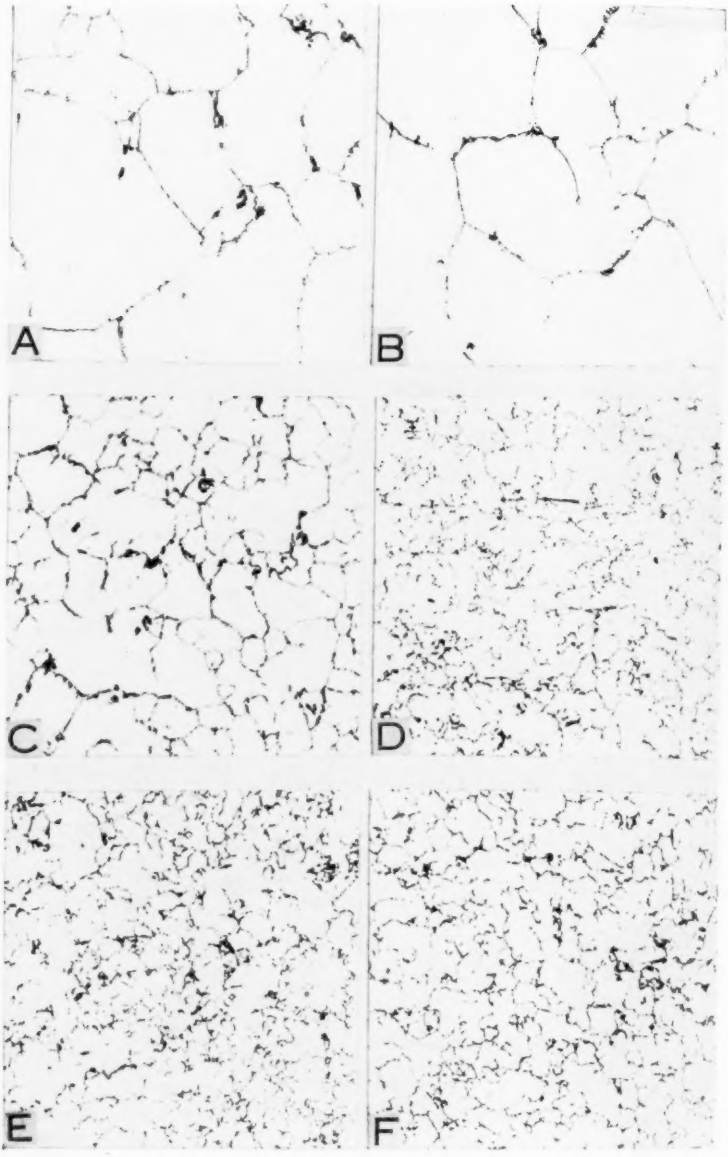

FIGURE 2.—*Grain size of the steels as developed by the McQuaid-Ehn test.*

Etched with boiling sodium picrate. ×100. The letters on the micrographs correspond with the designations used for the individual steels.

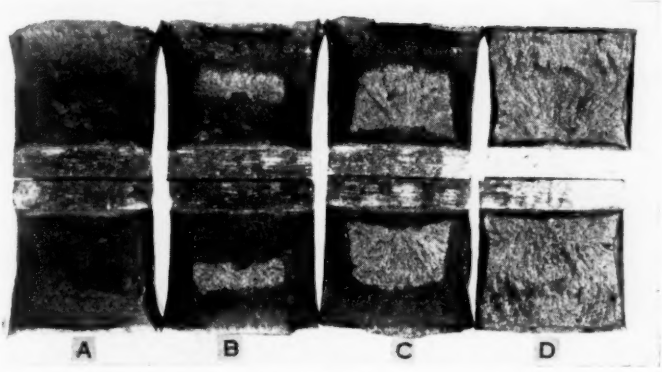

FIGURE 3.—*Appearance of typical Charpy impact fractures.* ×2.

A. Fibrous fracture obtained by testing specimen at a temperature above the cold-brittle range. Fracture was accompanied by considerable deformation and the energy absorbed was high.

B. Partly fibrous, partly granular fracture obtained by testing specimen at a temperature within the cold brittle range.

C. Partly fibrous, partly granular fracture obtained by testing specimen at a temperature within the cold-brittle range.

D. Granular fracture obtained by testing specimen at a temperature below the cold-brittle range. Fracture was accompanied by but little deformation, and the energy absorbed was low.

The austenitic grain sizes (table 2) were determined on bars 3 in. long, after heating at 1,475° F and 1,600° F and quenching one end into water. To eliminate variables in grain size, the procedure (rate of heating, time at temperature, etc.) was approximately the same as that employed during the heat treatment of the steels.

The specimens used for impact tests were 10 mm square by 55 mm long with a 45° V-notch 2 mm deep having a root radius of 0.25 mm. Since the shape of the notch can influence the impact properties of a specimen, particular care was exercised in grinding the cutter used for this work. All impact tests were made in quadruplicate at test temperatures of +100° C, room temperature, 0°, −20°, −40°, and −78° C in a Charpy machine having a capacity of 224 foot pounds. The constants of this machine and details of test procedure have been given in a previous paper [8].

III. RESULTS OF THE TESTS AND GENERAL DISCUSSION

Before proceeding to a discussion of the results of the tests, it is advisable to consider the meaning of the results of impact tests, particularly as modified by test temperatures.

It should be pointed out that any impact test is only qualitative, despite the fact that results are given numerical values indicative of the energy absorbed during the deformation and fracture of test specimens. The primary objective of impact tests of steels is to ascertain the relative tendency of different steels to fail in a brittle fashion, and this cannot be accomplished by making a few impact tests under one set of conditions. Slight changes in the size and shape of the test specimen, in the depth or sharpness of the notch, in total energy or velocity of the hammer, or in temperature, may cause disproportionate changes in the results of impact tests. At least one of these factors must be varied in order to obtain a true picture of the impact-deformation characteristics of any steel. The effects of these various factors and the interpretation of the results of impact tests are discussed by McAdam and Clyne [9] and by Hoyt [10].

The location of the temperature range wherein impact values are markedly decreased and the type of fracture changes from fibrous to granular (the cold-brittle range) is not a definite temperature range for any special steel. It may be moved to higher or lower temperatures merely by changing any one of numerous test variables. The *relative* tendency of a steel toward cold brittleness may, however, be established by studying the effect of test temperature upon the results of impact tests made under a certain set of test conditions. The temperature range in which cold brittleness occurs is an indication of the impact-toughness of the steel being tested. Under comparable conditions of test, the lower the temperature at which this transition occurs, the more dependable is that steel for engineering service. This statement is true despite the fact that a steel may absorb greater energy in impact at a temperature above and at one below the cold-brittle range than does another steel.

The appearance of the impact fractures obtained over a range of test temperatures, with all other factors constant, is an excellent guide to the impact-toughness of the steel under study. Typical fractures, shown in figure 3, are of three types. That shown in figure

3 (*A*), the fibrous or tough type, is accompanied by appreciable deformation and high energy absorption, and occurs at temperatures above the cold-brittle range. That shown in figure 3 (*D*) is of the granular or brittle type, is accompanied by little or no deformation and low energy absorption, and occurs below the cold-brittle range. Those shown in figure 3 (*B* and *C*) are typical of breaks which occur within the cold-brittle range. The relative areas of fibrous and granular appearance may vary widely, with concomitant variations in the

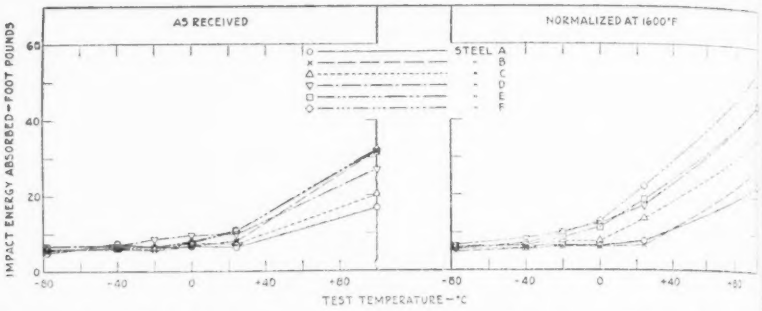

FIGURE 4.—*Effect of test temperature upon the impact-toughness of the steels as hot-rolled and as normalized.*

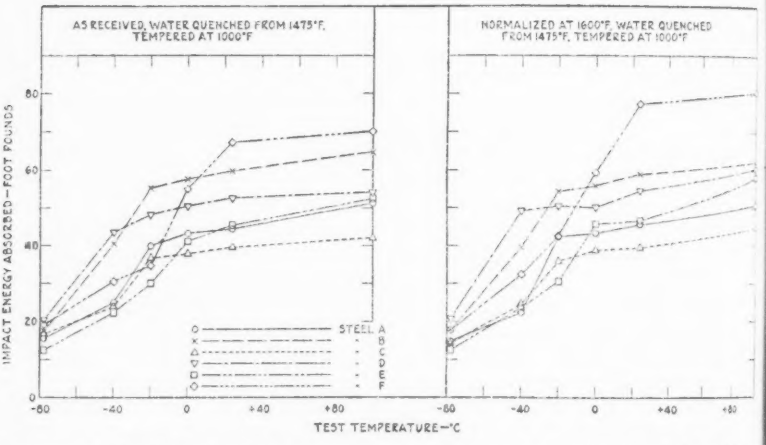

FIGURE 5.—*Effect of test temperature upon the impact-toughness of the steels as hardened and tempered at 1,000° F.*

impact-energy absorbed. The theory underlying the discontinuity of the transition from fibrous to granular fracture has been discussed by McAdam and Clyne [9].

The values obtained in impact tests at various temperatures are presented in several ways to show a comparison:

1. Between steels in the as-received condition and after normalizing at 1,600° F (fig. 4).

2. Of the effect of tempering at 1,000°, 1,150°, and 1,300° F on steels quenched from 1,475° F in both as-received and normalized conditions (figs. 5 to 7).

3. Of the effect of the various heat treatments on each steel individually (figs. 8 to 13).

Figure 4 shows that there was no significant difference between the impact resistance of the as-received and normalized steels at room temperature or below. The impact resistance was low, the fractures

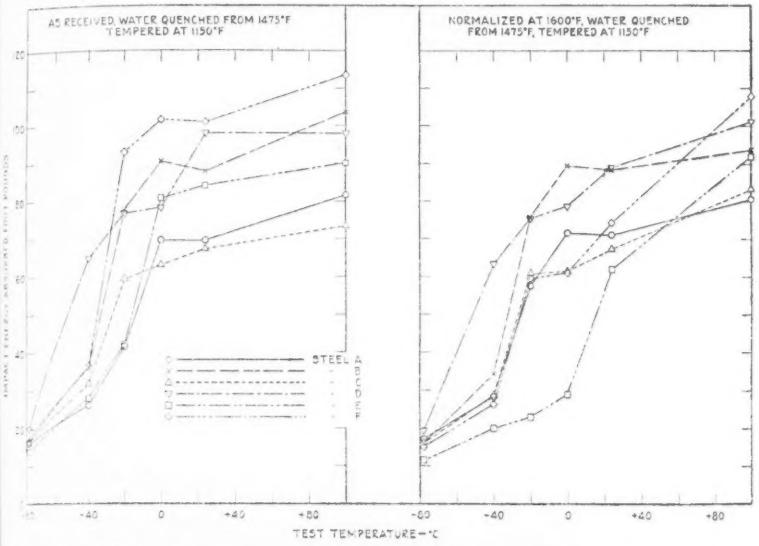
AS RECEIVED, WATER QUENCHED FROM 1475°F, TEMPERED AT 1150°F
NORMALIZED AT 1600°F, WATER QUENCHED FROM 1475°F, TEMPERED AT 1150°F
STEEL A B C D E F
-80 -40 0 +40 +80
TEST TEMPERATURE—°C

FIGURE 6.—*Effect of test temperature upon the impact-toughness of the steels as hardened and tempered at 1,150° F.*

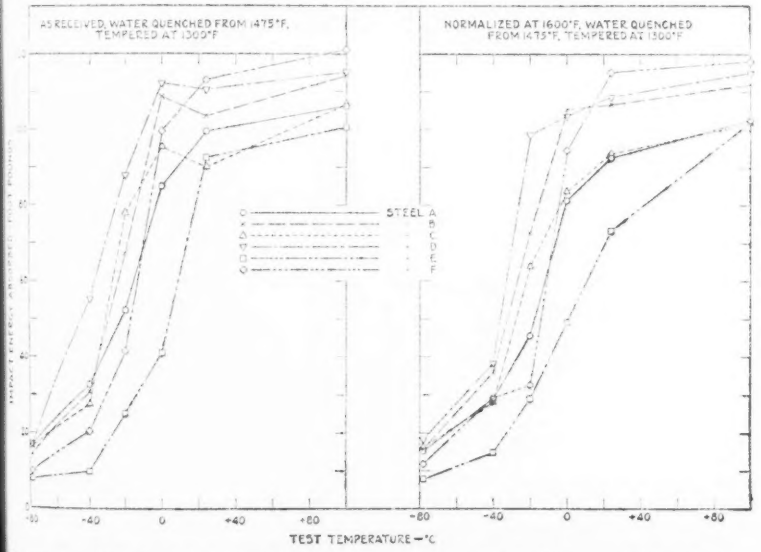
AS RECEIVED, WATER QUENCHED FROM 1475°F, TEMPERED AT 1300°F
NORMALIZED AT 1600°F, WATER QUENCHED FROM 1475°F, TEMPERED AT 1300°F
STEEL A B C D E F
-80 -40 0 +40 +80
TEST TEMPERATURE—°C

FIGURE 7.—*Effect of test temperature upon the impact-toughness of the steels as hardened and tempered at 1,300° F.*

were granular, and the cold-brittle range, as determined under the specific conditions of test, occurred above room temperature.

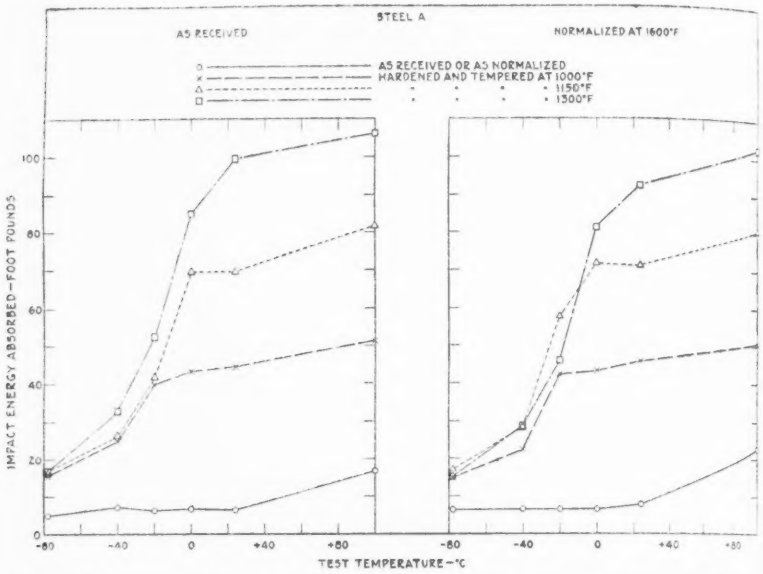

FIGURE 8.—*Comparison of the effect of different heat treatments upon the impact-toughness of steel A at different temperatures.*

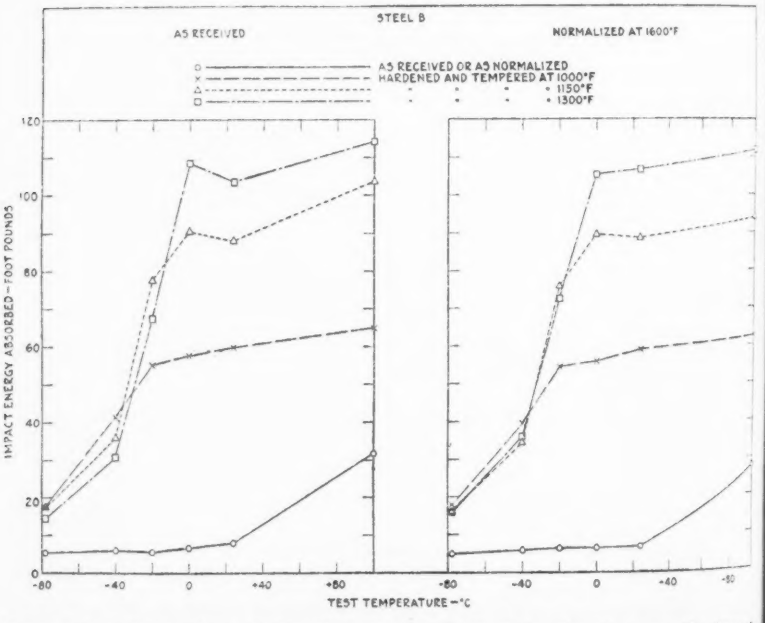

FIGURE 9.—*Comparison of the effect of different heat treatments upon the impact-toughness of steel B at different temperatures.*

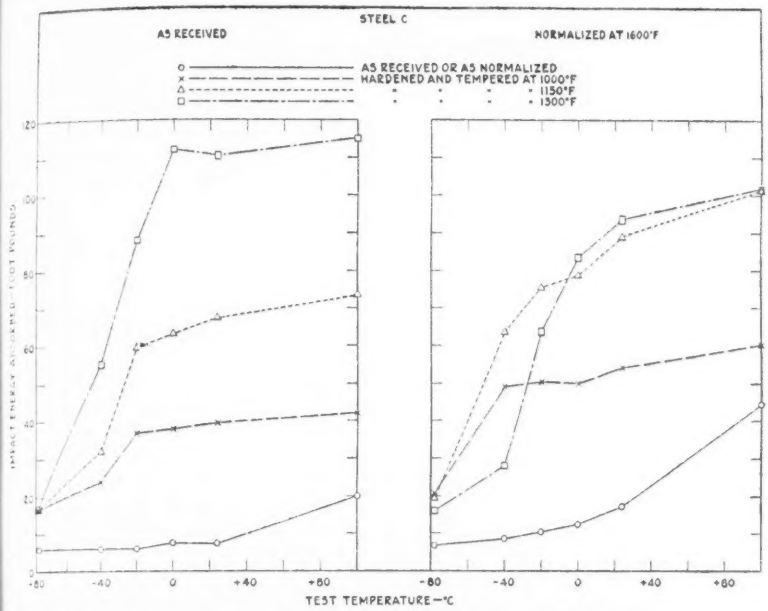
STEEL C
AS RECEIVED
NORMALIZED AT 1600°F
AS RECEIVED OR AS NORMALIZED
HARDENED AND TEMPERED AT 1000°F
" " " " 1150°F
" " " " 1300°F
IMPACT ENERGY ABSORBED - FOOT POUNDS
TEST TEMPERATURE - °C

FIGURE 10.—*Comparison of the effect of the different heat treatments upon the impact-toughness of steel C at different temperatures.*

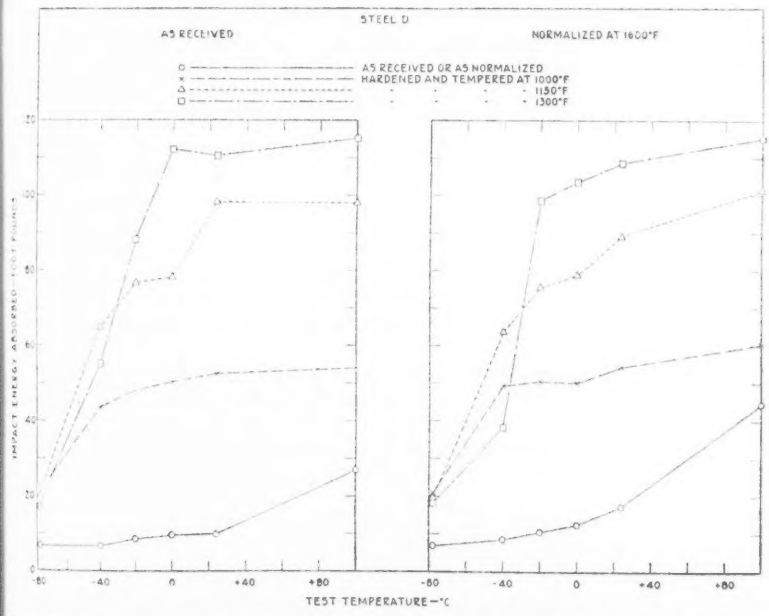
STEEL D
AS RECEIVED
NORMALIZED AT 1600°F
AS RECEIVED OR AS NORMALIZED
HARDENED AND TEMPERED AT 1000°F
" " " " 1150°F
" " " " 1300°F
IMPACT ENERGY ABSORBED - FOOT POUNDS
TEST TEMPERATURE - °C

FIGURE 11.—*Comparison of the effect of different heat treatments upon the impact-toughness of steel D at different temperatures.*

In the as-received condition all of the steels exhibited granular, or mostly granular fractures, at +100° C. In this condition, therefore, the cold-brittle range of all the steels occurred above +100° C.

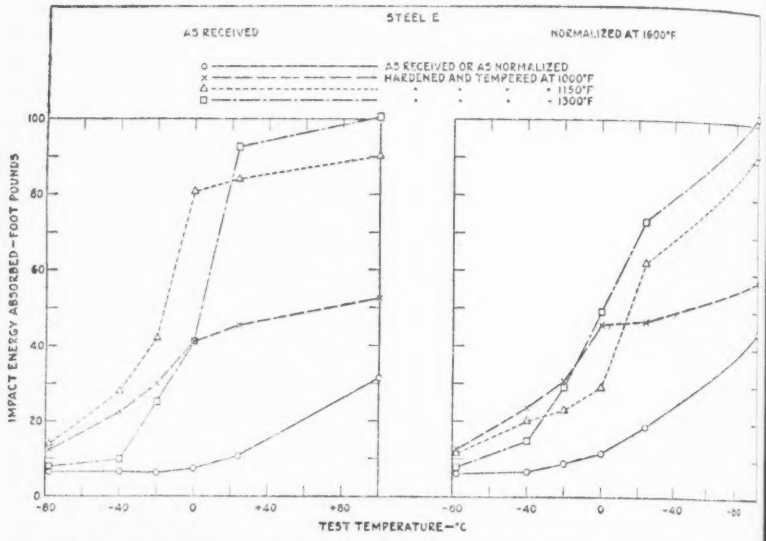

FIGURE 12.—*Comparison of the effect of different heat treatments upon the impact-toughness of steel E at different temperatures.*

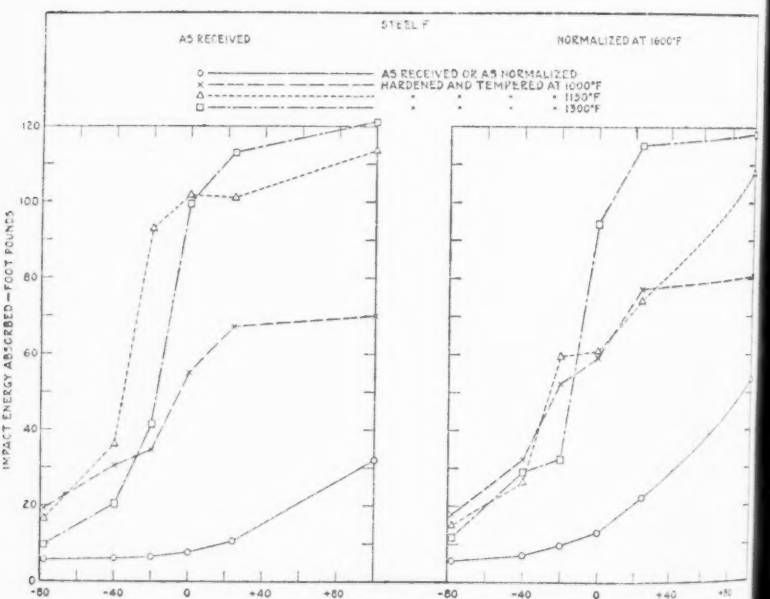

FIGURE 13.—*Comparison of the effect of different heat treatments upon the impact-toughness of steel F at different temperatures.*

In the normalized condition, steels *D*, *E*, and *F*, at +100° C, had fibrous fractures, high impact values, and the cold-brittle range, therefore, occurred between room temperature and +100° C. These steels had fine McQuaid-Ehn grain sizes (No. 8), as well as fine grain sizes at the normalizing temperature (also No. 8). Steel *C*, as normalized, had somewhat lower impact resistance at +100° C, the fractures were partly fibrous and partly granular, and the cold-brittle range occurred in the neighborhood of +100° C. This steel had a medium-fine McQuaid-Ehn grain size (No. 6), and at the normalizing temperature its grain size was No. 7. Steels *A* and *B*, both of which had coarse McQuaid-Ehn grain sizes (No. 3), exhibited granular fractures at +100° C, and the cold-brittle range, therefore, must be located at some temperature above +100° C. At the normalizing temperature, steels *A* and *B* had grain sizes of No. 5 and No. 4, respectively.

It is apparent that (1) normalizing caused an improvement in the impact-toughness of fine-grained SAE 1050 steel as compared with the same steel as hot-rolled, and (2) the impact-toughness of the normalized steels was related to both the McQuaid-Ehn and the austenitic grain size—the finer the grain size the greater the toughness. No relation between grain size and impact-toughness was apparent in the hot-rolled steels under the specific conditions of test. This type of steel (SAE 1050) does not, however, have appreciable impact-toughness in either the as-rolled or as-normalized conditions. This deficiency can be remedied by suitable heat treatment.

The effect of quenching from the proper temperature and tempering at relatively high temperatures was to lower markedly the temperature range within which cold-brittleness occurred (figs. 5, 6, and 7). None of the steels was cold-brittle at room temperature. In a few instances, cold-brittleness was manifested between room temperature and 0° C; but usually it did not occur above 0° C, and in many cases was observed only at temperatures lower than −40° C.

From figures 5, 6, and 7, it is obvious that the cold-brittle range of steel *D*, in all conditions of heat treatment, occurred at lower temperatures than in any of the other steels. This steel may therefore be considered to have the best impact-toughness, even though other steels sometimes had higher impact values at temperatures above the cold-brittle range. Steel *D* had a fine McQuaid-Ehn grain size and a fine austenitic grain size at the heat-treating temperature (1,475° F.). Steel *E*, however, with the same grain size as steel *D*, consistently exhibited the minimum impact-toughness, as measured by the location of the cold-brittle range, in all conditions of heat treatment.

Steel *B*, which generally showed the second-best impact-toughness, had a coarse McQuaid-Ehn grain size and a fine austenitic grain size (on the low side of No. 7) at the hardening temperature. Steel *A*, with the same grain sizes as steel *B*, however, had decidedly lower impact-toughness than steel *B* in the various conditions of heat treatment.

From the foregoing discussion it may be concluded that when heat-treated (1) there was no significant relation between grain size and impact toughness in SAE 1050 steel, and (2) each heat of SAE 1050 steel had its own characteristic resistance to impact. Another point to be emphasized is that high impact-toughness at room temperature

was no assurance of superior impact-toughness at lower temperatures. This is particularly well illustrated by the curves in figure 5, which show that steel *F* had higher numerical values for impact resistance when tested at room temperature than any of the other steels. When the impact-temperature curve is examined, however, it may be seen that cold-brittleness was manifested at higher temperatures in steel *F* than in steels *B* and *D*.

The curves in figures 8 to 13 illustrate the effect of heat treatment upon the impact-toughness of the individual steels at the various test temperatures. Normalizing prior to heat treatment had no beneficial effect upon the impact-toughness of any of the steels. At room temperature, maximum resistance to impact was obtained with specimens tempered at 1,300° F and minimum resistance with specimens tempered at 1,000° F. This condition did not always exist at lower test temperatures. The tempering temperature for maximum impact toughness, as judged by the impact-temperature curves, varied in the different steels. In general, the tempering temperature of 1,150° F seemed to impart maximum impact-toughness.

IV. SUMMARY AND CONCLUSIONS

A study was made of the effect of McQuaid-Ehn and austenitic grain sizes at heat-treating temperatures and of different heat treatments upon the low-temperature impact-toughness of six heats of SAE 1050 steel. Charpy impact tests, of standard Charpy V-notch specimens, were made at temperatures ranging from +100° C to −78° C. Under the specific conditions of test described, the following conclusions appear justified:

1. SAE 1050 steel, either as hot-rolled or as normalized, has low impact-toughness. In the hot-rolled condition this type of steel is cold-brittle at room temperature and the transition range to cold-brittleness occurs at temperatures above +100° C. Normalizing the hot-rolled steel improves the impact-toughness at room temperature and above, and the range of temperature at which cold-brittleness occurs is lowered, in some cases, to below +100° C.

2. Differences in grain size in the normalized steels appear to exert an influence on the impact toughness; the finer the McQuaid-Ehn or the normalized grain size, the lower is the temperature at which cold-brittleness is manifested. This trend was not observed, however, with the hot-rolled steels.

3. Impact-toughness is markedly improved by hardening and tempering, but normalizing prior to heat treatment has no effect upon this property.

4. Impact-toughness at room temperature is no criterion of impact-toughness at lower temperatures.

5. Fine grain size, either McQuaid-Ehn or austenitic, is no assurance of impact-toughness superior to that of coarser-grained steel similarly heat-treated (quenched and tempered), particularly as regards the occurrence of cold-brittleness.

6. SAE 1050 steel, in various conditions of heat treatment, does not have a characteristic resistance to impact in the same sense, for instance, as it has a characteristic tensile strength. Each individual heat, when heat-treated, apparently has an inherent resistance to impact between certain limits, and this is dependent upon factors not at present recognized.

V. REFERENCES

[1] Philip Schane, Jr., *Effects of McQuaid-Ehn grain size on the structure and properties of steel*, Trans. Am. Soc. Metals **22,** 1038 (1934).
[2] H. W. McQuaid, *Effect of McQuaid-Ehn grain size on hardness and toughness of automotive steels*, Trans. Am. Soc. Metals **22,** 1017 (1934).
[3] Howard Scott, *Factors determining the impact resistance of hardened carbon steels*, Trans Am. Soc. Metals **22,** 1142 (1934).
[4] E. S. Davenport and E. C. Bain, *General relations between grain size and hardenability and the normality of steels*, Trans. Am. Soc. Metals **22,** 879 (1934).
[5] S. Epstein, J. H. Nead, and T. S. Washburn, *Grain-size control of open-hearth carbon steels*, Trans. Am. Soc. Metals **22,** 942 (1934).
[6] C. H. Herty, Jr., *The effect of deoxidation on some properties of steel*, Trans. Am. Soc. Metals **22,** 113 (1934).
[7] F. B. Foley, *Résumé of round-table discussion on effect of sub-atmospheric temperatures on the properties of metals*, Trans. Am. Soc. Testing Materials **39,** 637 (1939).
[8] Samuel J. Rosenberg, *Effect of low temperatures on the properties of aircraft metals*, J. Research NBS, **25,** 673 (1940). RP1347.
[9] D. J. McAdam, Jr., and R. W. Clyne, *The theory of impact testing: Influence of temperature, velocity of deformation, and form and size of specimen on work of deformation*, Proc. Am. Soc. Testing Materials **38,** pt. 2, 112 (1938).
[10] S. L. Hoyt, *Notched bar testing*, Metals & Alloys **7,** 5, 39, 102, 140 (1936).

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RELATIONSHIP OF THE GARNET-HYDROGARNET SERIES TO THE SULFATE RESISTANCE OF PORTLAND CEMENTS

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ABSTRACT

Isometric $3CaO.Al_2O_3.6H_2O$, a constituent of set portland cement, is readily converted by sodium sulfate solutions to $3CaO.Al_2O_3.3CaSO_4.31.5H_2O$. Partial replacement of the Al_2O_3 in $3CaO.Al_2O_3.6H_2O$ by Fe_2O_3 or of the H_2O by SiO_2 gives "hydrogarnets" which are stable in the presence of sulfate solutions. Such substitutions may be brought about by inducing reactions between tricalcium aluminate hydrate and silica from various sources in the set cement or from added puzzolanic materials, and by increasing the content of glass and tetracalcium aluminoferrite in the cement.

Products having an X-ray structure nearly identical with that of grossularite garnet result when properly proportioned mixtures, made up of the puzzolanic material, dehydrated kaolin, with tricalcium silicate, or with lime and beta dicalcium silicate, are steamed at 500° C and 420 atmospheres.

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I. INTRODUCTION

Various investigators [1] [1] have demonstrated the existence of a general correlation between the potential tricalcium aluminate content of portland cements of low glass content and the resistance to sulfate action of mortars and concretes made from these cements. The typical reaction which occurs during sulfate disintegration in-

[1] Numbers in brackets indicate the references at the end of the paper.

volves conversion of the hydration products of tricalcium aluminate to gypsum and the "high-sulfate form" of calcium sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31.5H_2O$. This transformation is accompanied by considerable expansion which eventually may disrupt the specimen.

There are a number of methods by which the sulfate resistance of portland cement mortar or concrete can be increased, including the following:

(1) Steaming the mortar or concrete [2].

(2) Prolonged curing of the mortar or concrete at ordinary temperatures [3].

(3) Mixing the cement with a puzzolanic material [4].

(4) Increasing the glass content of the cement [5].

(5) Altering the chemical composition of the cement [3].

In view of the relationship between the tricalcium aluminate content and disintegration tendency of the cement, it seemed probable that these methods might be efficacious in the degree to which they convert the aluminate content of the set cement into a form not readily attacked by sulfate solutions. Recent work [6] suggested that this stabilized aluminate might consist of silica- or iron-containing hydrogarnet. Experiments which support this hypothesis have been made and are reported in this paper.

II. RESISTANCE OF HYDROGARNETS TO SODIUM SULFATE SOLUTION

1. METHOD OF TESTING

Samples of hydrogarnet preparations having compositions shown in figure 1 were available from a previous study. The isometric tricalcium aluminate hexahydrate (1, fig. 1), prepared by treating anhydrous tricalcium aluminate with steam at 150° C in an autoclave, was practically free from silica and ferric oxide. The tricalcium ferrite hexahydrate (8, fig. 1) was obtained by reaction of ferric chloride solution with boiling limewater. This preparation contained a certain amount of silica, probably combined as hydrated calcium silicate, since a determination of the unit cell size of the sample gave practically the theoretical value for $3CaO.Fe_2O_3.6H_2O$.

A sulfate test solution was desired which would contain a sufficient concentration of calcium ions to prevent undue hydrolysis of the hydrogarnet preparations placed in contact with it. Such a solution was prepared by mixing 100 g of anhydrous sodium sulfate with 1 liter of saturated lime solution (1.15 g of CaO per liter). The resulting mixture was slightly supersaturated with respect to gypsum and some precipitation of this compound occurred. To 100-ml quantities of the test solution, in tightly-stoppered flasks, 0.5-g samples of the hydrogarnet preparations were added. The flasks were allowed to stand with occasional daily shaking. Small samples of the solid phases were filtered off at intervals and examined microscopically.

2. RESULTS

Transformation of the $3CaO.Al_2O_3.6H_2O$ to well-developed needles of the "high-sulfate form" of sulfoaluminate, $3CaO.Al_2O_3.3CaSO_4.31.5H_2O$, began within a few hours and was complete after 2 days'

contact with the sulfate solution. The sulfoaluminate was unchanged by standing 6 months longer in contact with the solution.

The aluminate preparation containing no ferric oxide and only 7.7 percent of silica (2, fig. 1) was not perceptibly altered until after about 4 months when a very small amount of finely divided material having the mean refractive index of the sulfoaluminate appeared. This product increased to about 10 percent of the sample in 6 months. Preparations 4 and 5, fig. 1, which had Al_2O_3:Fe_2O_3 molar ratios of 2:1 (12.8 percent of Fe_2O_3) and 1:1 (18.4 percent of Fe_2O_3) and contained the lowest amounts of silica, showed a small amount of apparently amorphous material surrounding the isometric crystals after 6 months'

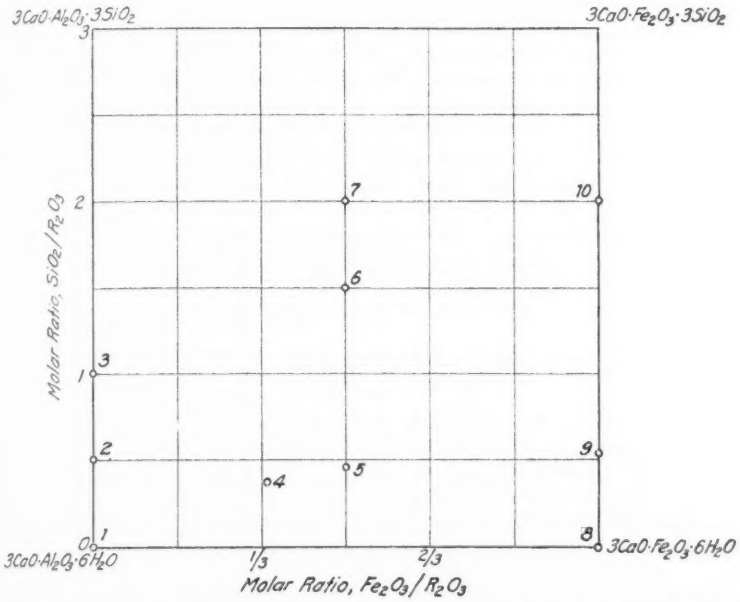

FIGURE 1.—*Compositions of members of garnet-hydrogarnet series exposed to sodium sulfate solution.*

contact with the sulfate solution. No appreciable alteration of any of the other preparations tested was observed during the 6-months' period.

Thus the hydrogarnets which contain 10 to 15 percent or more of either silica or ferric oxide appear to be very resistant to transformation by the sulfate test solution. It can be postulated, therefore, that the sulfate resistance of set portland cements will be greatly improved if the aluminate compounds which they contain are converted to silica- or iron-containing hydrogarnets. The remainder of this paper will attempt to show how this is accomplished by the various methods already mentioned.

III. EFFECT OF HYDROTHERMAL TREATMENT OF MIXTURES OF ALUMINATES AND SILICATES ON THE SULFATE RESISTANCE OF CEMENTS

1. METHOD OF STUDY

Mixtures of isometric $3CaO.Al_2O_3.6H_2O$ with definite amounts of various hydrated calcium silicates were prepared for treatment with water over a range of temperatures. A few mixtures of anhydrous tricalcium aluminate and the anhydrous calcium silicates were also included. The synthesis of the hydrated calcium silicates has been described in an earlier publication [7].

Some of the mixtures were placed in saturated lime solution (0.5 g of mixture in 200 ml of solution) at ordinary temperatures; the remainder were placed in high-pressure autoclaves and heated with sufficient water to insure the presence of liquid at the temperatures used. At the completion of the heating period samples of the solid phase were withdrawn, washed with alcohol and ether, and examined microscopically. From the relationship between index of refraction and composition in the $3CaO.Al_2O_3.6H_2O$-$3CaO.Al_2O_3.3SiO_2$ solid-solution series, given in fig. 2, the approximate composition of the isometric phase could be estimated from a determination of its refractive index. Fig. 2 was constructed from index of refraction values reported in the literature for $3CaO.Al_2O_3.6H_2O$, plazolite, and grossularite, and from values for two synthetic preparations obtained in this study.

2. PRODUCTS OF HYDROTHERMAL TREATMENT OF ALUMINATE SILICATE MIXTURES

Owing to the very different rates of reaction with water of the aluminate and silicate compounds in cement, it is probable that tricalcium aluminate hexahydrate will occur in set cement associated with hydrated calcium silicates of different compositions and stages of crystallization. However, if such products are unstable with respect to hydrated calcium aluminosilicates, further reactions may occur. Restricting consideration to mixtures having the molar ratio $1Al_2O_3$:$1SiO_2$, the following hypothetical equations may be formulated:

$$3CaO.Al_2O_3.6H_2O+SiO_2=3CaO.Al_2O_3.SiO_2.4H_2O+2H_2O. \quad (1)$$

$$3CaO.Al_2O_3.6H_2O+CaO:SiO_2:aq=3CaO.Al_2O_3.SiO_2.4H_2O+Ca(OH)_2+aq. \quad (2)$$

$$3CaO.Al_2O_3.6H_2O+2CaO.SiO_2.H_2O=3CaO.Al_2O_3.SiO_2.4H_2O+2Ca(OH)_2+H_2O. \quad (3)$$

$$3CaO.Al_2O_3.6H_2O+3CaO.SiO_2.2H_2O=3CaO.Al_2O_3.SiO_2.4H_2O+3Ca(OH)_2+H_2O. \quad (4)$$

According to figure 2, the index of refraction of $3CaO.Al_2O_3.SiO_2.4H_2O$ is approximately 1.63. Therefore, if the above reactions proceed to completion, the products will consist entirely of calcium hydroxide and an isometric phase of index 1.63. Table 1 shows that this condition is very nearly fulfilled in experiments 3, 6, 7, 8, and 11, where sufficient time had been allowed at the temperatures given, for complete transformation of the original materials. In most cases, the index of refraction of the isometric phase was not uniform but showed a variation of about 0.01 unit. This variation is probably caused by imperfect mixing of the original samples and by difficulty in obtaining

TABLE 1.—*Formation of silica-containing hydrogarnets from mixtures of aluminates and silicates*

Experiment number	Compounds mixed	Molar ratio Al_2O_3/SiO_2 in mixture	Temperature	Pressure	Time	Index of refraction of isometric phase in product	Other phases in product
			°C	*Atmospheres*	*Days*		
1	$3CaO \cdot Al_2O_3 \cdot 6H_2O + SiO_2$ gel	1:1	25	1	92	1.605	Amorphous, low-index material.
2	do	1:1	150	5	7	1.62	Do.
3	do	1:1	250	39	18	1.63 to 1.64	None.
4	do	1:2	350	163	10	1.67	Do.
5	$3CaO \cdot Al_2O_3 \cdot 6H_2O + CaO \cdot SiO_2$; aq [1]	1:1	25	1	54	1.605 to 1.61	Amorphous, low-index material.
6	do	1:1	150	5	7	1.625 to 1.635	$Ca(OH)_2$.
7	do	1:1	250	39	21	1.625 to 1.635	Do.
8	$3CaO \cdot Al_2O_3 \cdot 6H_2O + 2CaO \cdot SiO_2 \cdot H_2O$ [2]	1:1	250	39	34	1.63	Do.
9	$3CaO \cdot Al_2O_3 \cdot 6H_2O + 10CaO \cdot 8SiO_2 \cdot 6H_2O$ [3]	1:1	25	1	54	1.62 to 1.625	$10CaO \cdot 8SiO_2 \cdot 6H_2O + Ca(OH)_2$.
10	do	1:1	150	5	31	1.62 to 1.625	Do.
11	do	1:1	250	39	7	1.625 to 1.635	$Ca(OH)_2$.
12	$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaO \cdot SiO_2 \cdot 2H_2O$	1:1	25	1	62	1.61 to 1.62	$3CaO \cdot SiO_2 \cdot 2H_2O + Ca(OH)_2$.
13	do	1:1	150	5	32	1.62 to 1.625	Do.
14	do	1:1	250	39	10	1.62 to 1.63	Do.
15	$3CaO \cdot Al_2O_3 + \beta\text{-}2CaO \cdot SiO_2$	1:1	200	15	12	1.62 to 1.63	$10CaO \cdot 8SiO_2 \cdot 6H_2O + Ca(OH)_2$.
16	$3CaO \cdot Al_2O_3 + 3CaO \cdot SiO_2$	2:1	200	15	11	1.62	Do.
17	do	1:1	200	15	5	1.62 to 1.63	Do.
18	do	1:2	350	163	5	1.62 to 1.63	$3CaO \cdot SiO_2 \cdot 2H_2O + Ca(OH)_2$.

[1] Amorphous hydrated monocalcium silicate.
[2] Needle-form of dicalcium silicate hydrate, mean index of refraction 1.60 (see reference [7]).
[3] Orthorhombic dicalcium silicate hydrate, α=1.614, β=1.620, γ=1.633 (see reference [7]).

uniform reaction between crystals of low solubility. In experiment 3, a rise in index of refraction of the isometric crystals to as much as 1.64 may have been caused by a concentration of silica in the outer portion of the crystals. Numerous crystals having the higher indices of refraction contained cores of lower index.

A mixture of tricalcium aluminate hexahydrate and silica gel in the molar proportion $1Al_2O_3:2SiO_2$, treated with water at 350° C for 10 days, was completely converted to an isometric phase having an index of refraction approximately that of plazolite, $3CaO.Al_2O_3.2SiO_2.2H_2O$ (experiment 4).

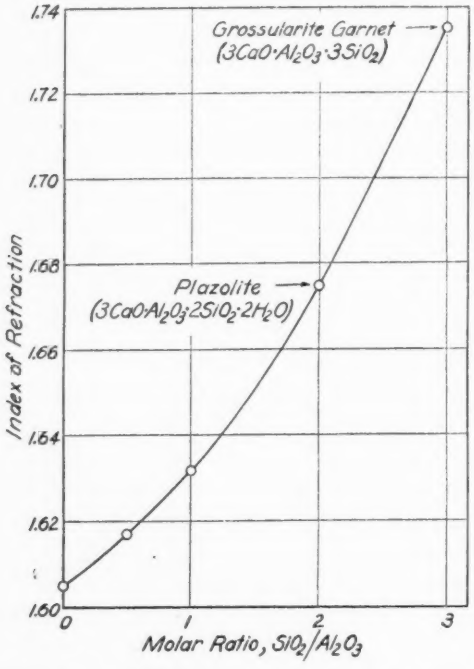

FIGURE 2.—*Relationship between index of refraction and composition in the solid-solution series* $3CaO.Al_2O_3.6H_2O-3CaO.Al_2O_3.3SiO_2$.

Mixtures of anhydrous tricalcium aluminate with beta-dicalcium and tricalcium silicates (experiments 15 to 18) gave reaction products similar to those of the hydrated compounds. The isometric phase in these preparations was formed in an extremely finely divided state. Variation of the ratio of aluminate to silicate had little effect on the index of refraction of the isometric product. With an excess of silicate present the temperature and duration of the experiment are the factors which determine the extent of substitution of silica in the isometric hydrated aluminate.

At room temperature, $3CaO.Al_2O_3.6H_2O$ reacts with hydrated dicalcium silicate (experiment 9) and hydrated tricalcium silicate (experiment 12) to form silica-containing hydrogarnets, whereas with silica gel (experiment 1) or amorphous hydrated monocalcium silicate (experiment 5), there is little evidence of such a reaction. It is possible that the amorphous reaction products in these experiments may form a layer of low permeability on the crystals of $3CaO.Al_2O_3.6H_2O$, thereby diminishing the rate of diffusion of silica into the aluminate.

3. RELATIONSHIP OF RESULTS TO CURING OF PORTLAND CEMENT MORTAR OR CONCRETE

It is well known that steam curing is one of the most effective means of increasing the sulfate resistance of portland cement mortars and concretes. The foregoing experiments show that the essential change produced by steam curing appears to be the removal from the set

cement of tricalcium aluminate hexahydrate, which is unstable in the presence of sulfate solutions, and the formation of a silica-containing hydrogarnet, which is stable in such solutions. The crystallization of hydrated calcium silicates and reduction in free calcium hydroxide, which accompany steam treatment, are probably factors of less importance. In curing at ordinary temperatures, the formation of silica-containing hydrogarnets may likewise be the determining factor. Both the rate of conversion of $3CaO.Al_2O_3.6H_2O$ and the improvement in sulfate resistance at such temperatures are very slow.

IV. EFFECT OF HYDROTHERMAL REACTIONS OF CEMENT COMPOUNDS WITH BURNT-CLAY PUZZOLANA ON THE SULFATE RESISTANCE OF CEMENTS

1. MATERIALS AND PROCEDURE

Dehydrated Georgia kaolin was selected as a typical burnt-clay puzzolana. The original material, before ignition, had the following composition (analysis by F. W. Glaze):

	Percent
SiO_2	45. 94
Al_2O_3	38. 22
Fe_2O_3	0. 45
TiO_2 (+ZrO_2, etc.)	1. 34
Ignition loss	13. 39

The kaolin was dehydrated by heating for 2 hours at 700° C. Mixtures of this material with various cement compounds were then prepared and treated with water at elevated temperatures and pressures. Microscopical examinations were made of the resulting products.

In two experiments the dehydrated kaolin was replaced by a coprecipitated alumina-silica gel having a molar ratio of $1Al_2O_3:2SiO_2$.

2. RESULTS OF HYDROTHERMAL TREATMENT

Hypothetical reactions of dehydrated kaolin with the various cement compounds in the presence of water may be represented by the following equations:

$$3CaO+Al_2O_3:2SiO_2+2H_2O=3CaO.Al_2O_3.2SiO_2.2H_2O \quad (1)$$

$$3CaO+3CaO.Al_2O_3+Al_2O_3:2SiO_2+8H_2O=2(3CaO.Al_2O_3.SiO_2.4H_2O) \quad (2)$$

$$CaO+\beta\text{-}2CaO.SiO_2+Al_2O_3:2SiO_2=3CaO.Al_2O_3.3SiO_2 \quad (3)$$

$$3CaO.SiO_2+Al_2O_3:2SiO_2=3CaO.Al_2O_3.3SiO_2 \quad (4)$$

Table 2 permits a comparison of the observed values for the index of refraction of the isometric phase with the theoretical index which would result from complete combination of the cement compound with the aluminum silicate. The values obtained in experiments 20, 22, 23, and 25 indicate that reactions 1, 2, 3, and 4, respectively, proceed almost to completion at the temperatures and with the reaction periods chosen.

Dehydrated kaolin was replaced by coprecipitated alumina-silica gel in experiment 21. Less of the isometric product was formed and

it was poorly crystallized compared with that of experiment 20. In a repetition of experiment 21, the coprecipitated gel was dehydrated at 700° prior to mixing with lime. The product of hydrothermal treatment in this case was somewhat better crystallized than that obtained from the undehydrated gel but the difference was not particularly marked.

TABLE 2.—*Formation of silica-containing hydrogarnets from mixtures of cement compounds and dehydrated kaolin*

Experiment number	Molar ratio of mixture	Temperature	Pressure	Time	Index of refraction of isometric phase in product		Approximate amount of isometric phase in product
					Observed	Theoretical (assuming complete reaction)	
		°C	*atm*	*Days*			*Percent*
19	$3CaO:Al_2O_3:2SiO_2$	150	5	14	1.64 to 1.65	1.675	70 to 80
20	do	350	163	11	1.65 to 1.66	1.675	80 to 90
21	do	350	163	11	1.64	1.675	50
22	$3CaO:3CaO.Al_2O_3:Al_2O_3:2SiO_2$	225	25	14	1.625 to 1.63	1.63	90
23	$CaO:\beta$-$2CaO.SiO_2:Al_2O_3:2SiO_2$	500	420	27	1.72	1.735	90
24	$3CaO.SiO_2:Al_2O_3:2SiO_2$	250	39	30	1.65	1.735	50
25	do	500	420	7	1.70	1.735	80

Well-crystallized preparations were obtained by steaming mixtures of beta-dicalcium silicate, lime, and dehydrated kaolin and of tricalcium silicate and dehydrated kaolin at 500° C and 420 atmospheres. The product of experiment 23, particularly, gave an X-ray pattern which showed practically no shift in lines from the pattern of grossularite garnet. The much slower rate of combination of dehydrated kaolin with tricalcium silicate at 250° C than at 500° C is illustrated by experiments 24 and 25.

3. APPLICATION TO PORTLAND-PUZZOLANA CEMENTS

The foregoing results cannot be applied directly to an explanation of the high sulfate resistance of portland-puzzolana cements because mortars and concretes made from such cements are usually not subjected to steam curing. Also the initial products of reaction of dehydrated kaolin with lime in the presence of water at ordinary temperatures are different from the isometric crystals obtained at elevated temperatures. As reported by Strätling [2] [8] and confirmed in unpublished work in this laboratory, the products at room temperature occur as hexagonal plates which are similar in appearance to the hexagonal forms of the hydrated calcium aluminates. These platelike crystals belong to a series of hydrated calcium silicoaluminates which appear to bear a close relationship to the calcium aluminate complex salts.

A sample of one of the hexagonal silicoaluminate preparations, exposed to the sulfate test solution, was about 50 percent converted to the sulfoaluminate in 10 days. After three weeks practically no hexagonal crystals remained. The hexagonal silicoaluminates, therefore appear to be much less resistant than the isometric calcium alumi-

[2] At the time of publication of a previous paper by the authors [6] they had read only a brief report of Strätling's work [9]. This report did not specify the crystalline nature of the product formed by the reaction of dehydrated kaolin with lime solution. It was assumed by the authors that the product might have been an isometric hydrated calcium aluminosilicate or "hydrogarnet." Strätling's publications show that this was not the case.

nosilicates (hydrogarnets) to transformation by the sulfate solution. This same experiment, however, indicates that the hexagonal compounds probably possess a higher solubility than the hydrogarnets and, if initially protected from sulfate action, should be gradually transformed to the hydrogarnets at ordinary temperatures. Such alteration would lead to increased sulfate resistance of the portland-puzzolana mortar.

V. EFFECT OF INCREASE IN GLASS CONTENT ON THE SULFATE RESISTANCE OF CEMENTS

In a previous paper [6], it was shown that glasses, representative of the compositions of various liquid phases formed in portland cement clinker at 1,400° C, will react with water at elevated temperatures to give hydrogarnets containing iron and silica. In order to ascertain whether or not similar reactions will occur at ordinary temperatures, powdered samples of three of the glasses used in the former study were made into pastes with 50 percent of their weight of water and stored in sealed vials. The three glasses had the following compositions:

	CaO	Al_2O_3	Fe_2O_3	SiO_2
	%	%	%	%
Glass *A*	58.3	33.0	0.0	8.7
Glass *B*	56.7	30.3	5.0	8.0
Glass *C*	54.8	22.7	16.5	6.0

After 2 months' storage, about 50 percent of glasses *A* and *B* had been converted to isometric crystals having indices of refraction of 1.62 and 1.62 to 1.63, respectively, and about 10 percent of glass *C* had altered to isometric crystals having a refractive index of 1.64 to 1.65. No separation of hematite or formation of hexagonal calcium aluminate hydrate was observed.

Increase of the glass content of portland cement clinker occurs partly at the expense of crystalline tricalcium aluminate, which is very susceptible to sulfate attack. Thus, reducing the content of tricalcium aluminate and increasing that of the glass, which will hydrate to silica- and iron-containing hydrogarnet, would be expected to improve the sulfate resistance of portland cement. Such improvement, with increase in glass content of cements, has been reported by Parker [5].

VI. EFFECT OF INCREASING ALUMINA–FERRIC OXIDE RATIO ON THE SULFATE RESISTANCE OF CEMENTS

Cements having a low alumina–ferric oxide ratio are considerably more resistant to sulfate action than those having a high ratio. Compositions of the former type are relatively high in potential tetracalcium aluminoferrite and low in potential tricalcium aluminate, whereas the reverse situation obtains in the latter type.

The much greater sulfate resistance of tetracalcium aluminoferrite than of tricalcium aluminate is explained by the fact, established in a previous study [6], that, when mixed with sufficient water to form a paste, the ferrite hydrates to give an iron-containing hydrogarnet while the aluminate hydrates to iron-free calcium aluminate hydrate. The unit cell size of the isometric phase obtained from a paste of tetracalcium aluminoferrite at room temperature was 12.60 A (angstroms), or 0.04 A higher than that of $3CaO.Al_2O_3.6H_2O$. The unit cube size of 3CaO.

$Fe_2O_3.6H_2O$ is 12.74 A, or 0.18 A higher than that of the aluminate. Since a linear relationship exists between unit cube size and composition expressed in mole percent in the series $3CaO.Al_2O_3.6H_2O$-$3CaO.Fe_2O_3.6H_2O$, a unit cube size of 12.60 A would correspond approximately to a solid solution containing $0.04/.018 \times 100 = 22$ mole percent of $3CaO.Fe_2O_3.6H_2O$ in 78 mole percent of $3CaO.Al_2O_3.6H_2O$. A sample of tetracalcium aluminoferrite steamed at 225° C gave an isometric product having a unit cube size of 12.62 A, corresponding to a solid solution of approximately 33 mole percent of $3CaO.Fe_2O_3.6H_2O$ in 67 mole percent of $3CaO.Al_2O_3.6H_2O$. Both of these solid solutions would be rather resistant to sulfate action.

VII. SUMMARY

Experiments on the constituents, and on the possible hydration products, of portland cement indicate that the sulfate resistance of portland cement should be increased by any method resulting in the removal from the set cement of tricalcium aluminate hexahydrate, which is unstable in sulfate solutions, and substitution for the aluminate of hydrogarnets containing iron or silica, which are stable in such solutions. Such substitution may be brought about by: (1) reaction of the hydrated aluminate with silica from the various silicates in the set cement, (2) addition of a puzzolanic material to the cement, and (3) increasing the glass and tetracalcium aluminoferrite contents of the cement.

Additional studies will be necessary to determine to what extent the members of the hydrogarnet solid-solution series are actually formed, or can be made to form in the setting and hardening of various cements and cement-puzzolana mixtures at ordinary temperatures.

Preparations having an X-ray structure nearly identical with that of grossularite garnet resulted when mixtures of beta-dicalcium silicate, lime, and dehydrated kaolin, and also of tricalcium silicate and dehydrated kaolin, were steamed at 500° C and 420 atmospheres.

The authors are indebted to H. F. McMurdie for making the X-ray patterns of the garnet preparations.

VIII. REFERENCES

[1] Carlson and Bates, Eng. News-Record **107,** 130–32 (1931). Gonnerman, Proc. Am. Soc. Testing Materials **34,** pt. 2, 244–302 (1934).
Bogue, Lerch, and Taylor, Ind. Eng. Chem. **26,** 1049–55 (1934).
Miller and Manson, Proc. Am. Soc. Testing Materials **40,** 988–1006 (1940).

[2] Miller, Proc. Am. Soc. Testing Materials **24,** pt. 2, 847–61 (1924); **30,** pt. 2, 636–53 (1930). Public Roads **5,** 203–12 (1927). Thorvaldson, Wolochow, and Vigfusson, Can. J. Research **6,** 485–517 (1932). Thorvaldson and Wolochow, J. Am. Concrete Inst. **9,** 241–65 (1938).

[3] Lea and Desch, The Chemistry of Cement and Concrete, p. 204 (Edwin Arnold and Co., London, 1935).

[4] Lea, Proc. of the Symposium on the Chemistry of Cements, Stockholm, 1938, 471–81 (Ingeniörsvetenskapsakademien, Stockholm, 1938).

[5] Parker, J. Soc. Chem. Ind. **58 T,** 203–13 (1939).

[6] Flint, McMurdie, and Wells, J. Research NBS **26,** 13–33 (1941) RP1355.

[7] Flint, McMurdie, and Wells, J. Research NBS **21,** 617–38 (1938) RP1147.

[8] Strätling, Ber. deut. keram. Ges. **20,** 522–27 (1939); Zement **36,** 427–32; 441–45; 455–60; 475–77 (1940).

[9] Büssem, Proc. of the Symposium on the Chemistry of Cements, Stockholm, 1938, p. 163, 497–98 (Ingeniörsvetenskapsakademien, Stockhlom, 1938).

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MICROSCOPIC STRUCTURE OF THE WOOL FIBER

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ABSTRACT

An investigation was undertaken to obtain information concerning the fine details of structure of wool fibers and especially of their constituent scale and cortical cells. Treatment of chemically modified wool with the enzyme, pepsin, was found to be an excellent method for releasing individual cells for such studies.

It is shown by microdissection that the striated appearance of the cortical cells is due to the presence of many fibrils which can be separated with microneedles. Near the center of each cell is a nucleus which has a granular structure. Between crossed nicols, the fibrillar part of the cortical cells appears birefringent, whereas the nucleus does not.

The scales show little internal organization such as exhibited by the cortical cells. When examined with crossed nicols they appear nonbirefringent. Unlike the cells of the cortex, the scales are not easily separated by treatment with enzymes, but remain attached to each other in a manner comparable to the arrangement of shingles on a roof.

A comparison of root and shaft of the fiber reveals numerous differences in reaction to microchemical color tests, as well as differences in cellular structure. The root, for example, gives a positive test for sulfhydryl groups whereas the shaft gives a negative test. Similarly, the shaft appears birefringent whereas the root does not. These and other observations clearly indicate that as the cells of the root emerge into the shaft a number of physical and chemical changes take place simultaneously.

When wool is placed in chlorine water, swellings arise on the surface of the fibers (Allwörden reaction). Evidence is presented in support of the view that these sacs arise solely from the scales and that their formation is associated with the reaction of the chlorine with disulfide groups of the cystine in the scales.

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I. INTRODUCTION

Wool fibers are specialized appendages of the epidermis of the sheep, and show many similarities to other skin tissues, such as nails, horns, and feathers. A growing fiber consists of a root and shaft, the former being the living region situated beneath the surface of the skin, whereas the latter is the nonliving portion that extends above the skin surface.

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.

Increase in length of the fiber is brought about by the proliferation of new cells in the root and the subsequent emergence of these cells into the shaft. The shaft is composed of dead cellular units which usually are arranged in three layers—an outer layer of scales, a middle region called the cortex, and a central core or medulla. The relative thickness of each of these layers varies considerably in different fibers. Kemp, for example, has a large medulla, whereas in the best grades of wool the medulla is either absent or very small.

Much of this knowledge of the structure of the fiber was contributed by the early researches of Nathusius [1][2] and McMurtrie [2]. These investigators obtained considerable information concerning the shape, length, and fineness of wool, and in addition described the various types of cells which comprise the fiber. A number of the structural details were also noted later by Kronacher and Lodeman [3], von Bergen [4], Reumuth [5], and Müller [6], as well as others. In the present investigation these earlier observations have been extended in order to obtain additional information on the fine details of structure of the fibers and especially of their constituent cells.

II. MATERIALS

Two samples of wool were used in the investigation. One consisted of domestic wool, for the most part nonmedullated, which was purified by successive extractions with ethyl alcohol and with ether for 16 hours each, followed by washing with water at 40° C. A second sample was obtained from the Bureau of Animal Industry, United States Department of Agriculture.[3] It consisted of wool carefully pulled from the back of a Hampshire sheep so as to have the roots attached to the shaft, and also of small pieces of skin, which were cut directly from the sheep and placed in fixing fluids.

III. EXPERIMENTAL PROCEDURE AND RESULTS

1. SEPARATION OF CORTICAL AND SCALE CELLS

When wool fibers are mounted in water and examined with a microscope, much can be learned about the size, shape, and appearance of the surface of the fibers, but very little is learned of the detailed structure of their constituent cells. In order to study the minute structure of the various types of cells, the fibers must be treated in a way that makes a more detailed microscopic examination possible. For this purpose thin cross and longitudinal sections can be employed to good advantage, but the liberation of single cells from the fibers is even more satisfactory.

The liberation of cells from fibers by various chemical reagents, enzymes, and bacteria has been frequently reported in the literature. The treatments with chemical reagents usually involve the use of strong acids or alkalies and are sufficiently drastic to produce more or less profound changes in structure. Treatment of the fibers with enzymes is in many respects more satisfactory and has been used considerably in the present investigation.

Although untreated wool is highly resistant to the action of enzymes, it has been shown in work now in progress in this laboratory [7] that

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] Acknowledgment is made to J. I. Hardy for supplying this material.

fibers in which disulfide cross-linkages have been ruptured by reduction with thioglycolic acid and then methylated to prevent re-formation of the linkages are rapidly attacked by treatment with an enzyme such as pepsin. Accordingly, it was decided to follow, microscopically, the changes which reduced and methylated wool undergoes in pepsin, in an effort to obtain information concerning the structure and behavior of the cells. For comparison, untreated fibers were similarly examined.[4] Samples of each were placed in vials containing a solution of the enzyme. At the same time, single fibers were placed in a drop of enzyme on a microscope slide and protected with a cover glass, which was sealed to the slide with vaseline. The latter method made possible the continuous observation of a single fiber over a relatively long period. The specimens were examined and fresh enzyme was added every 2 or 3 days. The experiments were run at two temperatures—one at room temperature (22° to 25° C) and another at 35° C. The material kept at the higher temperature was the first to show evidence of attack by the enzyme, but otherwise the two series ultimately presented essentially the same microscopic appearance.

In agreement with the other work [7], it was found that untreated wool was not readily attacked by pepsin. Even after long exposure to the enzyme these fibers showed little evidence of damage except for frayed ends, and sometimes the liberation of a few cortical cells. The reduced and methylated wool was attacked more rapidly. Cells obtained from this wool had the same initial appearance as cells obtained in a similar manner from untreated wool. However, as will be shown later, cells from untreated wool were resistant to further action of the enzyme whereas cells from reduced and methylated samples were eventually digested. With reduced and methylated wool, even at room temperature, changes in the fiber were detectable in less than 24 hours. The free ends of the fiber were usually frayed, and some intermediate parts appeared to be darkened and crushed. After several days pronounced changes had taken place. The fibers had lost their lustre and exhibited a pronounced striated appearance due to the increased prominence of the cortical cells. After continued treatment with enzymes, large numbers of cortical cells were liberated from the fibers (fig. 1, *A*, *B*, and *C*). The cortical cells were removed not only from the ends of the fiber but from intermediate parts as well, leaving in extreme cases practically intact tubes of scale cells (fig. 1, *C*). In regions where only part of the cortex was removed from a given area, it was found that the first cells to be liberated lay next to the scales. Additional cortical cells were released upon applying pressure to the cover glass.

The enzyme apparently had easier access to the cut ends of the fiber and thus brought about greater deterioration in those regions. This behavior has also been noted by other investigators. Photomicrographs by von Bergen [4] indicate that after certain chemical treatments the ends show the most damage. From the work of Royer and Millson [8] on dyed wool it is evident, also, that the ends of the fibers take up dye more rapidly than do intermediate parts. Similar results, indicative of the greater liability to attack at the ends, were

[4] A solution of pepsin was prepared by dissolving 1 mg of the crystalline enzyme in 1 ml phosphate buffer at pH 1.2. A few drops of merthiolate were added to the solution as a preservative.

obtained in the present investigation. Furthermore, when the ends of untreated and of reduced and methylated fibers were sealed with glue before placing the fibers in pepsin, it was found that the breakdown of the fibers was retarded. After a few weeks in the enzyme, however, this difference between fibers with sealed and with unsealed ends was lost, both samples then showing similar degrees of disintegration.

In order to study further the action of pepsin on untreated and on reduced and methylated wool, cross sections, cut 10 to 15 microns thick with the Hardy device [9], were placed either in vials containing the enzyme or in drops of the latter on microscope slides. Even after a month there were only slight changes in the untreated sections (fig. 2, *A*). With sections of reduced and methylated wool the cortex was eaten out, leaving in extreme cases only a thin ring of scales (fig. 2, *C*). The degree of breakdown of the wool was related to the length of exposure to the enzyme (compare fig. 2, *B*, with fig. 2, *C*). Furthermore, the rate of digestion appeared to be associated with the extent of reduction of the wool, as reduced and methylated fibers with 90 percent of the disulfide cross-linkages broken were much more rapidly attacked by the enzyme than those in which only 50 percent of the linkages had been disrupted. When free cortical cells, released from partially reduced and methlyated fibers upon treatment with pepsin, were placed in fresh enzyme for a period of 1 month, some of the cells appeared to be digested whereas others from the same sample remained practically intact. These differences appear to be associated with the extent of reduction of the wool and suggest that the undigested cells may be ones in which most of the cross-links are intact.

The results of these experiments indicate that the scale cells are resistant to the action of pepsin and that the ease with which single cortical cells are liberated depends on the previous chemical treatments which the fibers received. Although cortical cells may be rapidly separated from each other by the action of pepsin, individual cells show further signs of disintegration only after continued treatment with the enzyme.

2. STRUCTURE OF THE CORTICAL CELLS

Single cortical cells are spindle-shaped. They vary in size depending on the sample of wool. Walther [10] found that their average size varied from 80 to 110 microns in length, 2 to 5 microns in width, and 1.2 to 1.6 microns in thickness. Cortical cells liberated from fibers by the action of chemical agents frequently show evidence of fimbriated ends. In most cases, also, the cells are prominently striated.

On careful examination of single cells liberated from the cortex by the action of pepsin, a structure located near the center of the cell and resembling a nucleus was frequently observed (fig. 3, *A*). This central region did not, however, stain with common nuclear dyes such as hematoxylin and methylene blue. Figure 3 (*A*) shows also that the nucleus is granular, whereas the rest of the cell is fibrillar in appearance.

Nuclei are not easily observed in untreated cross sections, but are clearly visible after the latter have been properly stained or swollen [5].

For example, treatment of the sections with pepsin, sodium carbonate, or with a combination of both these reagents rendered the outline of individual cortical cells and their nuclei distinct (fig. 4). Furthermore, when the cells were treated with Orange II [5] (a dye which readily stains wool) the cells became deep orange, but this central region was only lightly stained. Upon examination with crossed nicols, a dark, central, elongated area was nearly always detectable in the bright cell (fig. 3, *B*). In other words, each birefringent cortical cell possesses a nonbirefringent nucleus. Finally after continued treatment with pepsin, many of the cortical cells were nearly eaten in two at the middle (fig. 3, *C*), even though the cell is widest at this point. This suggested that the nucleus consists of a material which is more readily attacked by the enzyme than is the rest of the cell.

The structural details of the cortical cells were further investigated by dissecting them with the aid of a micromanipulator. Upon careful manipulation it was possible to insert two fine glass needles into a single cell and pull it apart. When this was done, it was found that the cell was composed of many fibrils (fig. 5, *A*, *B*, and *C*). When examined between crossed nicols, the latter appeared to be birefringent. Small and large groups of fibrils were dissected from the cell, and in some cases all the fibrils were spread out in the form of a fan. By this technique it was possible to prove that the striated appearance of the cortical cells is due to the presence of fibrils and not merely to surface irregularities or diffraction phenomena.

3. STRUCTURE OF THE SCALE CELLS

As already described, the scales, unlike the cells of the cortex, were not appreciably affected by pepsin. They usually remained attached to each other in the form of tubes (fig. 1, *A*, *B*, and *C*) corresponding to their arrangement in intact fibers, or at least in rather large groups, which furnished excellent material for a microscopic examination. The liberation of single scale cells was relatively infrequent, nor were additional ones readily released upon applying pressure to the cover glass. Although the scales stained poorly, the addition of a dye such as Orange II was helpful in showing their arrangement. It was clear after staining that the scales overlapped in a manner comparable to the arrangement of shingles on a roof (fig. 6). Except for a few indistinct markings on the surface, individual scales showed little evidence of internal structure.

When handled with microneedles, groups of scales freed by the action of pepsin appeared to be rather pliable, although the individual scale cells were not easily separated from each other. They could, nevertheless, be torn apart in such a way as to form chunks of scale material. In so doing there was no obvious fibrillar structure such as that shown by the cortical cells.

When the Feulgen test for nucleic acid (see section III–4) was applied to untreated wool fibers, the scale cells of the shaft gave a negative test. Scales liberated from the fibers by various treatments were also examined in an effort to detect nuclei. Although structures superficially resembling nuclear bodies were observed occasionally in these cells, their presence could not be demonstrated clearly nor consistently.

[5] A 1.4-percent solution of Orange II at pH 1.5 was used.

Scales released by treatment with acids, alkalies, enzymes, or by mechanical scraping were examined between crossed nicols. In all cases, the scales, both before and after staining, showed practically no birefringence.

Additional information concerning the structure of the scales is contained in the section on the Allwörden reaction.

4. DIFFERENCES BETWEEN ROOT AND SHAFT

Since the cells of the root are alive and growing, whereas the cells of the shaft are dead, it is not surprising to find profound physical and chemical differences between these two regions of the fiber. Several of these differences were revealed when microchemical color tests were applied to wool fibers a short time after they had been carefully pulled from the back of a sheep so as to have the roots attached to the shaft.

These fibers were stained according to Feulgen's technique [11, 12], which is considered to be specific for nucleic acid. A positive test is indicated by the red coloration obtained when a fuchsin-sulfurous acid solution is applied to the nucleus. Fibers which had been given this test showed a root which was stained deep red, whereas the shaft remained colorless (fig. 7). This difference could be detected even with the unaided eye. Upon mounting the stained fibers in a medium of higher refractive index and examining with a microscope, individual nuclei were observed (fig. 8). At the base of the root the nuclei and cells were relatively large and more or less rounded. Farther from the base the nuclei and cells were elongated. In some cases the nuclei were very narrow and slit-like, although distinctly red. A little below the level where the fiber emerges from the skin there was a rather abrupt change in the reaction of the nuclei, that is, they gave a negative Feulgen test in the shaft. That this difference did not appear to be caused by poor penetration of the dye into the shaft was indicated by the fact that fibers from which the scales had been removed by mechanical treatment still failed to give a positive test.

In order to study further the changes which take place as the cells pass from the root to the shaft, longitudinal sections were made of pieces of sheepskin with fibers attached. The tissue was embedded in a mixture of paraffin and cellulose acetate [13], cut into sections according to the usual cytological procedure, and then stained either with hematoxylin or according to the method of Feulgen. The cells of the root had a somewhat roundish shape and a more or less granular appearance. The cells of the shaft, on the other hand, were elongated and distinctly fibrous. These facts are undoubtedly related to observations made with crossed nicols, which show that the shaft of the fiber is birefringent whereas the birefringence of the root is negligible. In agreement with the results obtained with single fibers, the nuclei in the cells of the root were found to give a positive reaction to Feulgen's test. Nuclei were observed in those cells of the root which gave rise to scales as well as in those which gave rise to cortical cells.

When a single fiber was mounted in dilute ammonium hydroxide and treated with sodium nitroprusside, a pink to red color was developed in the root, whereas the shaft of the fiber remained colorless (fig. 9). The red coloration obtained with sodium nitroprusside

indicates that at least some of the sulfur in the root is present in sulfhydryl form. This is in agreement with the findings of previous investigators [14, 15, 16, 17, 18], who showed that the sulfhydryl-containing substance is limited to the living cellular parts of the epidermis and its appendages. In order to be sure that the difference in reaction between the root and shaft was not caused merely by a differential rate of penetration of the reagent, the scales were mechanically removed from a few fibers. The results with such fibers were in agreement with those obtained in the original test.

The biuret test for proteins, the Sakaguchi test for arginine, and the Millon and Pauly tests for tyrosine were also applied to single fibers. These tests did not reveal any differences between the root and shaft, except that the former gave a positive test more quickly.

The differences between the root and shaft may be summarized as follows:

Root	Shaft
Soft and easily crushed.	Tough and horny.
Cells roundish.	Cells elongated.
Positive test for nucleic acid.	Negative test for nucleic acid.
Nuclei stained with hematoxylin.	Nuclei unstained with hematoxylin.
Cytoplasm granular in appearance.	Cells distinctly fibrous.
Not birefringent.	Birefringent.
Positive test for sulfhydryl groups.	Negative test for sulfhydryl groups.
No Allwörden reaction with chlorine water.	Many large Allwörden "sacs".

5. ALLWÖRDEN REACTION

When wool fibers are placed in chlorine water, the so-called Allwörden reaction takes place [19, 20]. This treatment causes the formation of sacs [6] on the surface of the fiber (fig. 10, *A* and *B*). That the formation of these sacs is in some way associated with the scales has been suggested by many investigators [5, 19, 20, 21, 22, 23]. It is not clear, however, from a review of the literature, whether the sacs arise solely from the scales or whether the latter are merely pushed out by the swelling of a layer of material which lies beneath them. Since this is pertinent to an understanding of the structure of the fibers, the reaction was investigated in detail.

Although sacs form quickly with saturated chlorine water, their formation is slowed down by the use of dilute solutions. Likewise, the reaction is retarded, or even completely inhibited, by certain types of damage to the fiber. The first evidence of sacs is the appearance on each scale of a small swelling which gradually increases in size until the sac involves the entire scale surface. Incipient swelling did not appear to be confined to a particular part of the scale, such as base or tip. In a few cases two or more foci of swelling occurred in a single scale and were observed to flow together to form one large sac. It was also evident from the experiments that the size and shape of the sacs was associated with similar properties of the scales.

The sacs usually appeared optically empty. After certain treatments, however, particles showing Brownian movement were observed in them. As described by Kronacher and Lodemann [3], these particles were especially numerous when fibers which had been stained

[6] Since the swellings are shown to be protein membranes filled with liquid, "sac" is believed to be a more appropriate descriptive term than "bubble," which is in widespread use in the literature.

with picric acid were placed in aqueous methylene blue subsequent to their treatment with chlorine water. In agreement with the observations of Kronacher and Saxinger [22], it was found that the thin membrane of a sac could be stroked with a needle of the micromanipulator without causing the sac to burst, but just as soon as the microneedle pierced the membrane the sac collapsed, leaving small bits of the membrane still attached to the fiber. Likewise, the sacs collapsed after prolonged treatment with chlorine water, and after exposure to certain chemical agents, especially alkalies (fig. 11). The sacs were stained by dyes, such as methylene blue and malachite green, and this treatment was helpful in studying their size and shape.

When cross sections about as thick as the length of the scales of wool fibers were treated with chlorine water, typical sacs were formed. The latter appeared to arise superficially on the surface of the scales. There was no swelling of the region just inside the scales, such as might have been expected if some part of the fiber in addition to the scales was directly involved in the formation of sacs. Although the results of this experiment, as well as some observations with intact single fibers, suggest that the scales alone give rise to sacs, this fact could not be demonstrated clearly by these techniques.

In untreated wool the scales are closely appressed to one another (fig. 12, *A*). In carrying out some preliminary experiments during the course of this investigation, however, it was noted that certain chemical treatments loosened the scales and caused them to bend away from the fiber. For example, when wool fibers were placed in concentrated sulfuric acid for an hour or less, or in concentrated formic acid for several weeks, the scales were loosened in a way which resembled warped shingles on a roof (fig. 12, *B*). After prolonged treatment with these acids, single scales, or small groups of scales, were completely separated from the fibers. Scales which had been loosened or liberated in this way were excellent for studying the origin of the sacs. After removal from the acid, the fibers were washed with distilled water and then placed in chlorine water. Sacs formed quickly, and in agreement with the conclusions of Müller [6], it was evident that they came from the scales alone. It was clear, also, that the sacs were formed between the upper and lower surfaces of each individual scale cell. A small swelling first appeared somewhere in the scale, and then increased in size until the whole scale was swollen to resemble a little ellipsoidal bag (fig. 12, *C*). Both the upper and lower surfaces of a sac appeared to be of approximately equal thickness. After their formation, the sacs on loose scales showed the same behavior to dyes and chemical reagents as the sacs on fibers which had not been treated with acids. In cases where the scales were loosened from each other but not bent away from the fiber, the formation of sacs aided in the further separation of the scales. Sometimes sacs were formed on completely isolated scales; at other times where only fragments of single scales were treated with chlorine, sacs were not formed although the two layers of the scale were seen to separate. Apparently in the latter instance true sacs could not form because of the torn edges of the scales. The relationship between the formation of sacs in untreated and in acid-treated fibers is shown diagrammatically in figure 13.

Chlorine water caused the formation of sacs on all parts of a wool fiber except the root (fig. 14). Tests on hairs from more than a score

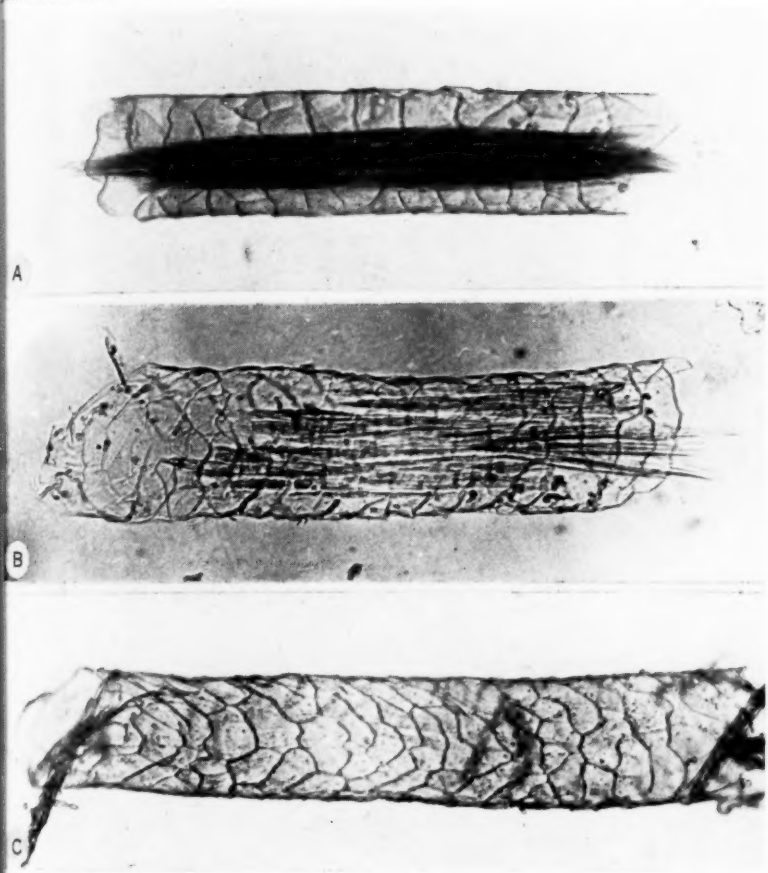

FIGURE 1.—*Reduced and methylated wool fibers treated with solutions of pepsin.*

A, *B*, and *C* show three stages in the removal of cortical cells from the fibers. *A* and *B* unstained; *C* stained with Orange II. Magnification ×350.

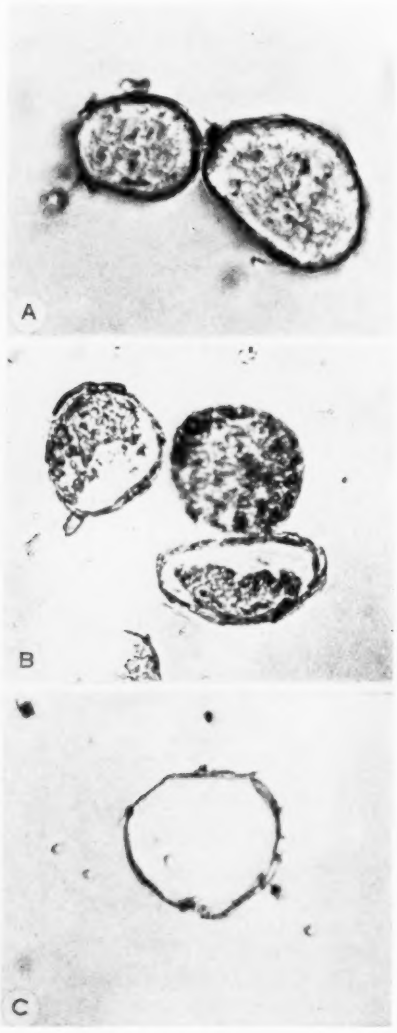

FIGURE 2.—*Cross sections of wool fibers treated with solutions of pepsin.*

A, Sections of untreated fibers in pepsin for 1 month. *B*, Sections of reduced and methylated fibers in pepsin for 10 days. *C*, Section of reduced and methylated fiber in pepsin for 1 month, showing only the thin ring of scales which remains. Magnification ×450.

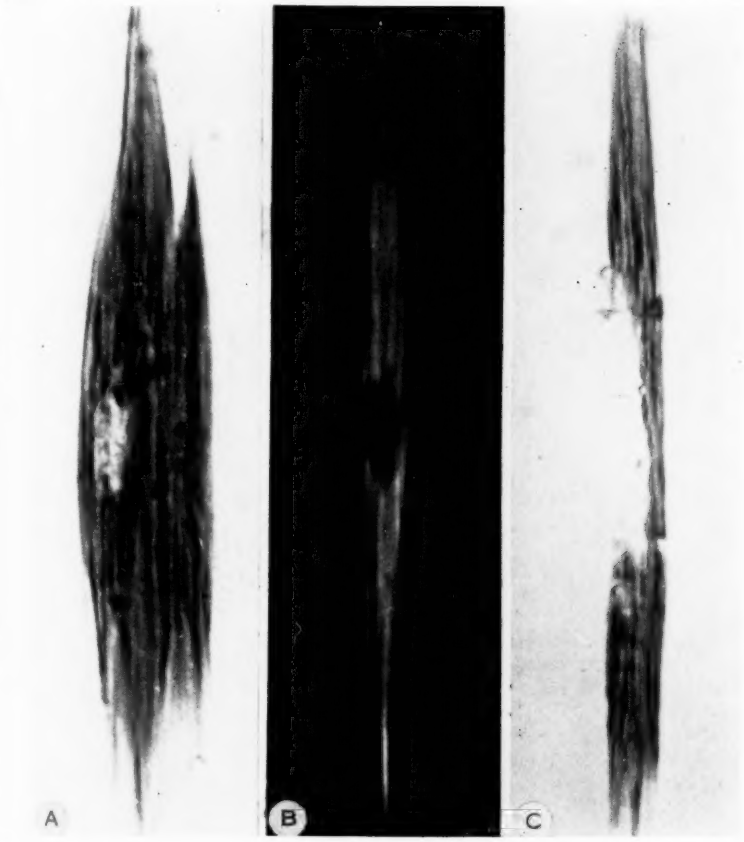

FIGURE 3.—*Single cortical cells from reduced and methylated fibers photographed under various conditions.*

A, Cell, stained with Orange II, showing the nucleus and the fibrillar appearance of the rest of the cell. *B*, Cell, between crossed nicols, showing the nonbirefringent nucleus in the birefringent cell. *C*, Single cell nearly eaten in two by the prolonged action of pepsin. Magnification ×1,400.

FIGURE 4.—*Cross section of an untreated wool fiber after several weeks in a solution of pepsin followed by swelling with 9-percent sodium carbonate.*

The photomicrograph shows the outline of the individual cortical cells and their nuclei. Magnification ×1,500.

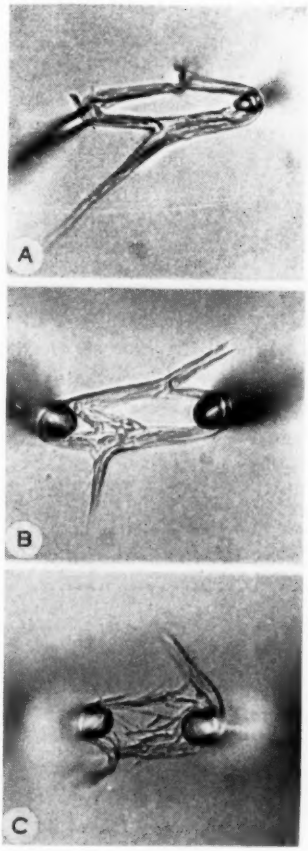

FIGURE 5.—*Cortical cells being dissected with microneedles to show their fibrillar structure.*

Magnification ×500.

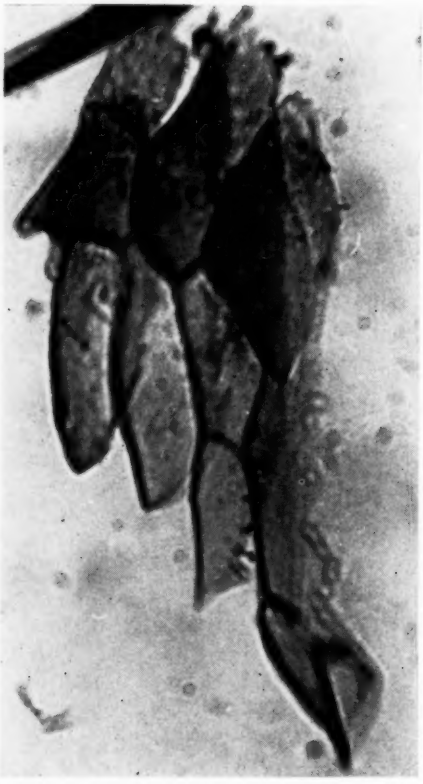

FIGURE 6.—*Group of scales released by the action of pepsin on reduced and methylated fibers.*

Stained with Orange II. Magnification ×1,420.

FIGURE 7.—*Single fiber (recently pulled from the back of a sheep) stained according to Feulgen's technique, showing the dark-colored root indicative of a positive test for nucleic acid.*

Fiber mounted in water. Magnification ×120.

FIGURE 8.—*Root of a wool fiber showing individual nuclei in the cells of the root.*
Fiber stained according to the technique of Feulgen and mounted in tricresyl phosphate. Magnification ×500.

FIGURE 9.—*Single fiber (pulled from the back of a sheep) treated with sodium nitroprusside.*

The dark color of the root indicates the presence of sulfhydryl groups. Part of the cuticle of the follicle remains attached to the fiber. Magnification ×120.

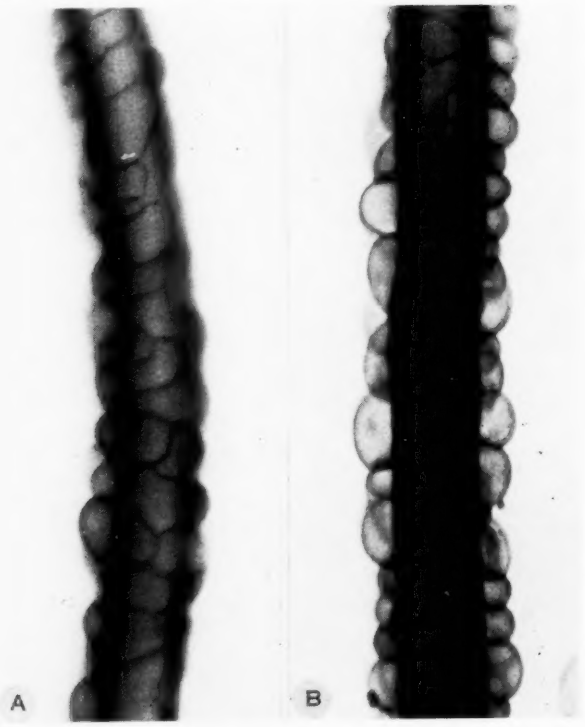

FIGURE 10.—*Fibers treated with saturated chlorine water to give the Allwörden reaction.*

A, Surface view of a fiber after sac formation. *B*, Fiber in focus approximately midway between its upper and lower surfaces. Fibers stained with aqueous methylene blue. Magnification ×500.

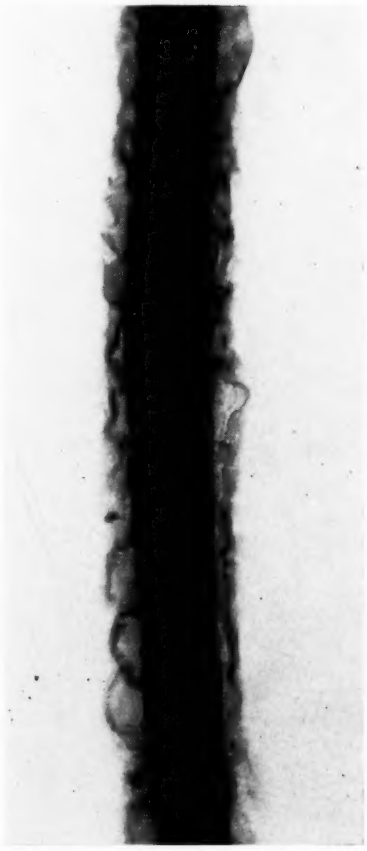

FIGURE 11.—*Effect of alkali on Allwörden sacs.*

Single fiber treated with chlorine water, methylene blue, and then 1-percent sodium hydroxide, showing the collapsed sac membranes at the surface of the fiber. Magnification ×500.

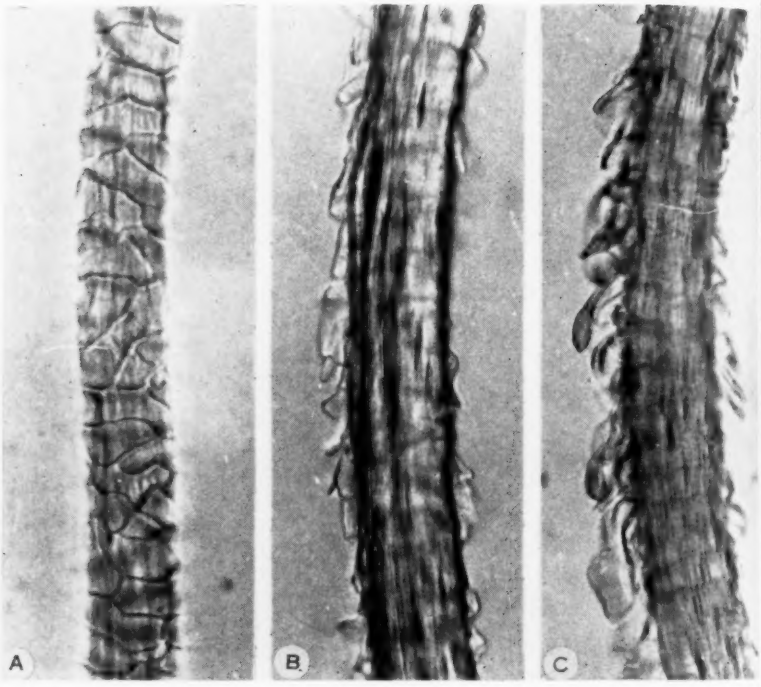

FIGURE 12.—*Scales and their relation to the formation of Allwörden sacs.*

A, Fiber mounted in water and photographed in surface view to show the arrangement of the scales. *B*, Fiber treated with concentrated sulfuric acid to loosen scales. *C*, Fiber treated with sulfuric acid to loosen the scales, and then with chlorine water to form sacs. The photomicrograph shows several sacs in various stages of formation, each arising from an individual scale. Magnification ×425.

FIGURE 14.—*Fiber showing root and part of the shaft, after treatment with chlorine water.*

Many sacs arise in the shaft but none in the root. Magnification ×120.

FIGURE 15.—*Fibers showing swellings in the cortex after treatment with acid and chlorine water.*

A, Wool fiber after 2 hours in concentrated sulfuric acid followed by treatment with chlorine water. *B*, Wool fiber after 14 months in concentrated formic acid followed by treatment with chlorine water. Similar results were obtained with fibers that had been boiled in the acid for about 4 hours. Magnification ×450.

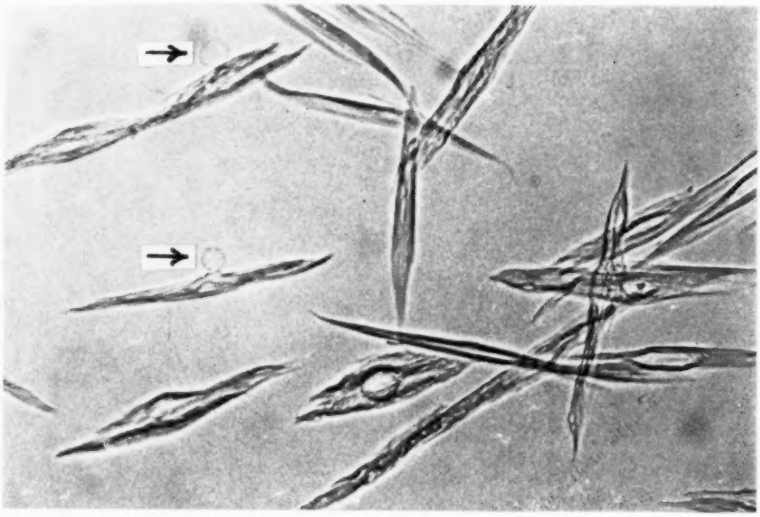

FIGURE 16.—*Individual cortical cells showing swollen nuclei after treatment with chlorine water.*

The cells were released by the prolonged action of concentrated formic acid, and then, after washing in distilled water, treated with chlorine. Arrows indicate additional swellings which sometimes arise from the nucleus. Magnification ×420.

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of common and rare animals were, likewise, found to give the Allwörden reaction.

In order to study further the conditions necessary for the formation of Allwörden sacs on the scales, untreated wool was placed in a 0.6-percent solution of sodium carbonate at 50° C. At various intervals thereafter, samples of the wool were removed, washed in acid and in water, and finally placed in chlorine water. The number, size, and rapidity of formation of the sacs was observed microscopically. It was found that sac formation was retarded with increasing length of alkali treatment. Mark [24] has similarly shown that the number of sacs formed on a fiber by chlorine water was decreased as the concentration of the carbonate and the temperature at which the reaction was carried out were increased. In the present investigation, chemical analysis of the fibers showed that as the cystine content of the fibers decreased, because of the action of the carbonate, sac formation was retarded. Similarly, samples of wool which were degraded by photochemical reactions showed poor sac formation. The extent of the sac formation varied with the duration of the irradiation. Samples of wool degraded in this way also had appreciably reduced cystine contents [25, 26]. The Allwörden reaction was also tried on samples of wool in which the mode of linkage of the sulfur had been altered by treatments such as reduction and alkylation. In all cases the sacs were formed more quickly when the cystine content was high, whereas the formation of sacs did not occur when the cystine content was lowered sufficiently. While not all of the above chemical treatments are specific for cystine in wool, it is significant, nevertheless, that samples of wool with low cystine contents fail to give the Allwörden reaction. The results suggest that the formation of sacs is dependent on the specific reaction of chlorine with unaltered disulfide groups of the cystine in the scales of the fiber. That chlorine can react with cystine has already been demonstrated [27]. A possible mechanism is that the disulfide linkages are split and oxidized to strongly acid groups such as perhaps sulfonic acid groups. An osmotic type of swelling could then take place to form the sacs noted. Further evidence favoring this view is obtained when concentrated salt solutions are added to the fibers after the reaction with the chlorine. Under these conditions the sacs contract.

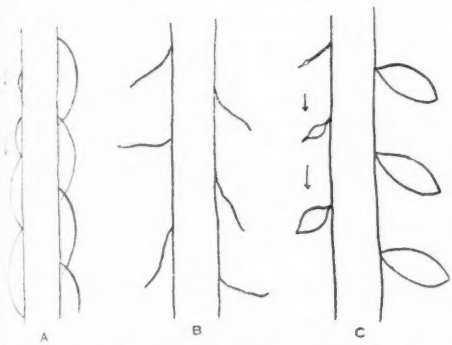

FIGURE 13.—*Diagram illustrating, in longitudinal view, the formation of sacs.*

A, The origin of sacs in intact fibers. *B*, The separation of scales upon treating intact fibers with sulfuric acid. *C*, The origin of sacs on single scales which have been separated by the treatment with acid. Arrows indicate an increase in size of the sacs.

It was noted, during the course of the above experiments with acid-treated wool, that when the scales gave rise to typical sacs, localized swellings often appeared in the cortex (fig. 15, *A* and *B*). In order to study this phenomenon further, wool fibers were treated with acid for

longer periods in order not only to loosen the scales but to release individual cortical cells as well. Fibers which had been placed in concentrated sulfuric acid at room temperature for 1 to 2 hours, or in boiling concentrated formic acid for about 6 hours, were found to be suitable for these experiments. Individual cortical cells released by these treatments showed distinct signs of swelling when placed in chlorine water. It was obvious, moreover, that the swelling in each cell was confined principally to the nucleus (fig. 15, *B*, and fig. 16). In some cases additional swellings appeared to arise as buds from the swollen nucleus (fig. 16). Swollen nuclei were not observed in fibers which had been treated with alkali or other reagents which prevent the Allwörden reaction. Although the foregoing observations suggest that the typical Allwörden reaction of the scales and the swelling cortical nuclei may be related phenomena, additional experiments pointed to dissimilarities between the two. In the presence of concentrated salt solutions, for example, the scale sacs became flaccid, and upon replacing the salt solution with water they regained their former turgidity; the nuclear swellings on the other hand failed to react in this way. Furthermore, a gentle prick with the tip of a microneedle was sufficient to bring about the collapse of scale sacs, whereas this did not occur when nuclear swellings were punctured.

IV. REFERENCES

[1] W. V. Nathusius, Das Wollhaar des Schafes (Berlin, 1866).
[2] W. McMurtrie, Wool and Other Animal Fibers (Government Printing Office, Washington, 1886).
[3] C. Kronacher and G. Lodemann, Technik der Haar und Wolleuntersuchung (Berlin, 1930).
[4] W. von Bergen, American Wool Handbook (American Wool Handbook Publishing Co., New York, N. Y., 1938).
[5] H. Reumuth, Klepzig's Textil-Z. **21,** 352 and **34,** 495 (1939).
[6] C. Müller, Zellforsch. Mikroskop. Anat. [A] **29,** 1 (1939).
[7] W. B. Geiger, W. I. Patterson, L. R. Mizell, and M. Harris. (Publication in preparation).
[8] G. L. Royer and H. E. Millson, Am. Dyestuff Reptr. **29,** 697 (1940).
[9] J. I. Hardy, U. S. Dept. of Agriculture Circular 378 (1935).
[10] A. R. Walther, Landw. Jahrb. **55,** 531 (1920–21).
[11] R. Feulgen and H. Rosenbeck, Z. physik. Chem. **135,** 203 (1924).
[12] C. E. McClung, Handbook of Microscopical Technique (Hoeber, New York and London, 1939.
[13] C. M. Barlow, J. Text. Inst. **29,** T111 (1938).
[14] E. Buffa, J. physiol. path. génér. **6,** 645 (1904).
[15] E. Walker, J. Physiol. **59,** 32 (1924).
[16] E. Walker, Biochem. J. **19,** 1085 (1925).
[17] G. H. Perceval and C. P. Stewart, Brit. J. Dermatology and Syphilis **42,** 215 (1930).
[18] P. Wels, Archiv exptl. Path. Pharmakol., **188,** 265 (1938).
[19] v. Allwörden, Studien über Einwirkung von Chlor auf Schafwolle. Diss. Berlin (1913).
[20] v. Allwörden Z. angew. Chem. **29,** 77 (1916).
[21] P. Krais and P. Waenting, Z. angew. Chem. **33** (1920).
[22] C. Kronacher and G. Saxinger, Z. Tierzücht. Züchtungsbiol. Tierernähr. **4,** 30 (1925) and **5,** 3 (1926).
[23] W. Spöttel, Melliands Textilber. **6,** 605 (1925).
[24] H. Mark, Einzeldarst a. d. Kaiser-Wilhelms Institut f. Faserstoffchem. 1 (1925).
[25] H. A. Rutherford and M. Harris, J. Research NBS **23,** 597 (1939) RP1255.
[26] M. Harris and A. L. Smith, J. Research NBS **19,** 563 (1938) RP 1091.
[27] M. Harris and A. L. Smith, J. Research NBS **17,** 577 (1936) RP928.

WASHINGTON, May 8, 1941.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1413

Part of Journal of Research of the National Bureau of Standards, Volume 27, August 1941

BEHAVIOR OF CALCIUM SULFATE AT HIGH TEMPERATURES

By Edwin S. Newman

ABSTRACT

Differential heating curves were used to study the behavior of calcium sulfate at high temperatures. After cooling, the material was examined by means of the petrographic microscope and by study of its X-ray pattern. It was found that the beta-to-alpha transition of calcium sulfate occurs at approximately 1,214° C, and the conclusion of its discoverer that the high temperature form is unstable was confirmed. There appears to exist a eutectic mixture of alpha $CaSO_4$ and CaO which melts at approximately 1,365° C. The reported existence of basic sulfates of calcium was not confirmed.

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I. INTRODUCTION

The behavior of pure calcium sulfate is of interest in considering the properties of those types of calcium sulfate cements or plasters which are prepared by heating the raw material to a very high temperature. Several plants are in existence abroad at which calcium sulfate is used as one of the raw materials for the manufacture of portland cement and sulfuric acid, advantage being taken of the decomposition of calcium sulfate to lime and sulfur trioxide at high temperatures. This decomposition is presumably responsible in part for the absence of $CaSO_4$ in many portland cement clinkers made in the ordinary way, as has been reported recently by the National Bureau of Standards [1].[1]

Naturally occurring calcium sulfate is found in two forms, as gypsum with 2 molecules of water of crystallization and as anhydrite containing no water of crystallization. By heating gypsum at successively higher temperatures four modifications can be prepared in order as follows: (1) the hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$, of which plaster of paris is largely composed; (2) an extremely hygroscopic anhydrous form known as soluble anhydrite which changes rapidly to the hemihydrate in the presence of water vapor; (3) an anhydrous modification identical with the naturally occurring anhydrous calcium sulfate mentioned above; (4) and at approximately 1,200° C a high-temperature form

[1] Figures in brackets indicate the literature references at the end of this paper.

stable, except for decomposition, only at this and higher temperatures [2]. At such temperatures the decomposition of $CaSO_4$ to CaO and SO_3 becomes appreciable. The total equilibrium pressure of SO_3, SO_2, and O_2 over calcium sulfate has been measured [3, 4] and found to be approximately 100 mm at 1,225° C. The decomposition pressure increases rapidly with increase of temperature, and extrapolation of Marchal's data [3] indicates that it probably reaches 1 atmosphere in the neighborhood of 1,400° C. The presence of 30 percent of alumina, 43 percent of silica, or 35 percent of kaolin lowers the decomposition temperature [3] to about 1,350°, 1,275°, and 1,150° C, respectively. This is presumably responsible in part for the absence of calcium sulfate [1] in many portland cement clinkers, since the total equilibrium pressure of SO_3, SO_2, and O_2 over a mixture containing calcium sulfate, silica, and alumina may be expected to be several atmospheres at clinkering temperatures.

The transition of the ordinary forms of anhydrite to the high-temperature modification was reported to occur at 1,196° C by Grahmann [2], who studied the material by means of a petrographic microscope equipped with a furnace for maintaining the sample at high temperatures. Abrupt changes in interference colors observed when a single crystal was heated and the appearance of the crystal on cooling served, together with heating and cooling curves, to identify a transition and fix its temperature. Masuda [5] reported that this transition occurred at 1,232° C, and unpublished data obtained by the writer indicated that the transition took place at an intermediate temperature. Because of the large variation in the reported temperature of transition, it was decided to report these data together with further studies of the behavior of calcium sulfate at elevated temperatures and of the system CaO—$CaSO_4$.

II. MATERIALS

Artificial anhydrite, $CaSO_4$, was prepared by heating $CaSO_4 \cdot 2H_2O$ of analytical reagent quality for 1 hour at 600° C. Natural anhydrite from Midland, Calif., was ground to pass a No. 200 sieve. Analyses indicated that the mineral contained 0.15 percent of SiO_2, 0.15 percent of $Al_2O_3 + Fe_2O_3$, and 0.06 percent of MgO. The loss on ignition was 1.6 percent, including 0.9 percent of CO_2. Calcium carbonate of reagent quality was used for a source of lime in preparing mixtures of $CaSO_4$ and CaO. These mixtures were prepared by stirring the artificial anhydrite and calcium carbonate together in the desired proportions with sufficient distilled water to form a slurry, which after thorough mixing was evaporated to dryness and ground in an agate mortar to pass a No. 100 sieve. Subsequently the mixtures were ignited at 950° C for 2 hours to remove carbon dioxide.

III. PROCEDURE

Heating and cooling curves were obtained by means of a differential thermocouple of Pt:Pt–10-percent Rh in a small vertical tube furnace. The $CaSO_4$ and Al_2O_3 as the reference material were placed, respectively, in two small semicircular crucibles, ½ inch in outside diameter and 1 inch deep, with a capacity of about 2 g of powdered material. The two hot junctions of the differential thermocouple were embedded

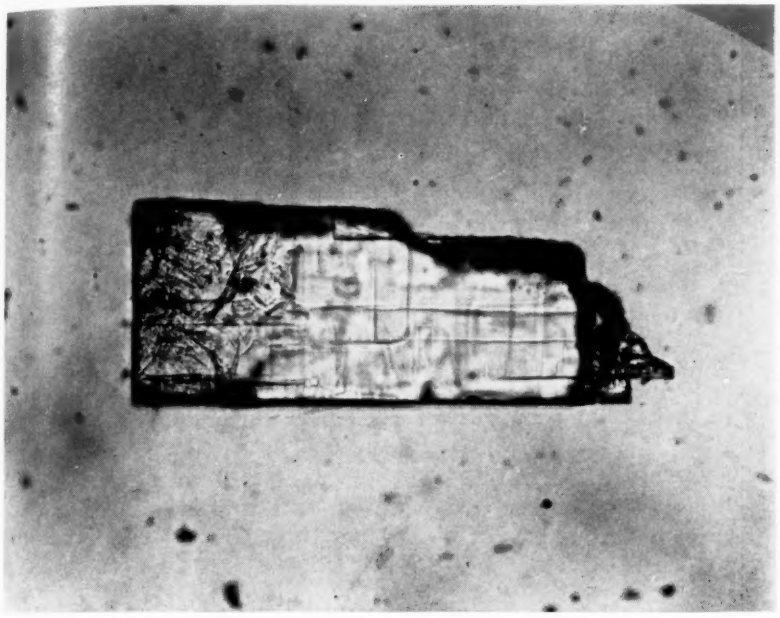

FIGURE 1.—*Crystal of anhydrite after heating 10 minutes at 1,213° C; ×50.*

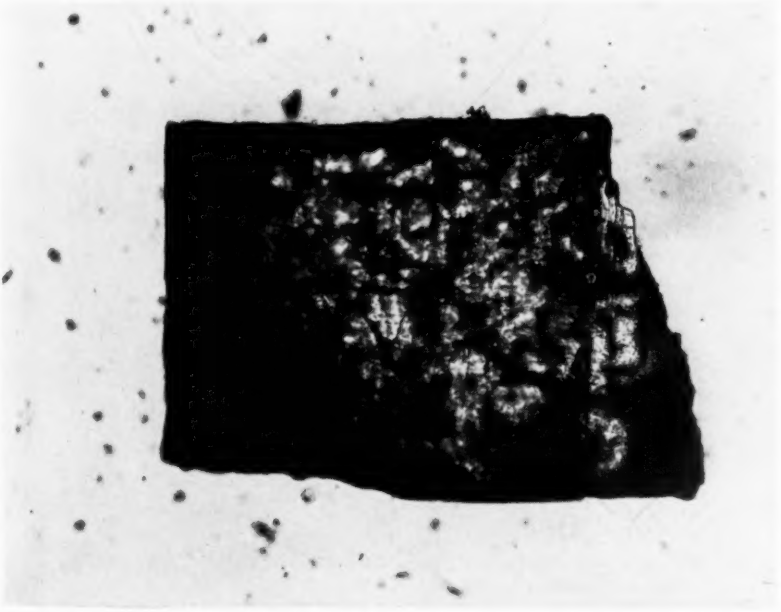

FIGURE 2.—*Crystal of anhydrite after heating 10 minutes at 1,217° C; ×50.*

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in the two materials and the crucibles suspended in the furnace. The emf developed by the hot junction in the $CaSO_4$ was measured by means of a precision potentiometer, and differences in temperature between the two hot junctions were indicated by the deflections of a galvanometer. The rates of heating or cooling, which were maintained constant during the series of readings taken for any one heating curve, ranged from 2° to 5° C per minute. The potentiometer reading and the deflection of the galvanometer were recorded every minute, or oftener if they were changing rapidly. A few small charges wrapped in platinum foil were heated and then quenched in water or mercury. These samples were then examined by means of the petrographic microscope and by study of their X-ray patterns. The thermocouples were calibrated by the Bureau, and the differential thermocouple was checked occasionally against the melting point of $CaO \cdot B_2O_3$ (1,154° C) [6] and the beta-to-alpha transition of $2CaO \cdot SiO_2$ (1,420° C) [7].

IV. RESULTS AND DISCUSSION

The results are given in table 1. Examination of these data shows that the reversible transition of the ordinary form of anhydrite to the high-temperature modification occurs at approximately 1,214° C. The presence of large amounts of CaO (up to 76 percent) did not appear to alter this temperature significantly. The temperature at which the transition occurs was further substantiated by the following procedure. Fragments of natural anhydrite were heated for 10 minutes at 1,210° to 1,220° C, cooled, and examined. Although heating below 1,214° C caused no visual change, higher temperatures caused the particles to become opaque and under the microscope they were seen to be made up of crystallites at random orientation. This change is illustrated by photomicrographs taken by ordinary transmitted light of two such fragments after heating, one at 1,213° C (fig. 1) and the other at 1,217° C (fig. 2). The crystallites appeared to be the ordinary or beta form. Attempts to obtain alpha calcium sulfate at room temperature by quenching samples heated above the transition temperature were unsuccessful.

Another reversible thermal effect occurs on heating anhydrite to still higher temperatures. Frequently this is not found the first time the material is heated but is manifested upon cooling, and thereafter the deflections of the galvanometer become more pronounced as the heating and cooling cycles are continued. The average temperature at which this thermal effect appeared on heating artificial anhydrite was 1,371° C. Natural anhydrite gave a somewhat lower value, owing perhaps to the presence of the other materials indicated by the analysis. Considerable supercooling occurs; the average temperature at which the breaks occurred in the cooling curves was 1,340° and 1,329° C for the artificial and natural anhydrites, respectively. This thermal effect corresponds to the inflection which Grahmann [2] occasionally found in the cooling curve at 1,320° to 1,370° C.

In the present work the appearance of the contents of the crucible after heating was not uniform, but in many cases the anhydrite appeared to have fused when the temperature had at no time exceeded 1,390° C. Since the temperature at which the thermal effect occurred was not greatly altered by the presence of large amounts of lime, the conclusion was drawn that it is caused by the melting and freezing of

TABLE 1.—*Temperature of alpha-beta transition and of eutectic melting observed with calcium sulfate and with calcium sulfate–lime mixtures*

Natural anhydrite [a]				Artificial anhydrite [b]				Calcium sulfate–lime mixtures [c]						
Transition temperature		Eutectic temperature		Transition temperature		Eutectic temperature		CaO [d]	Transition temperature		Eutectic temperature		CaO after heating	
From heating curves	From cooling curves	From heating curves	From cooling curves	From heating curves	From cooling curves	From heating curves	From cooling curves		From heating curves	From cooling curves	From heating curves	From cooling curves		
°C	°C	°C	°C	°C	°C	°C	°C	%	°C	°C	°C	°C	%	
1,213	1,193	1,345	1,314	1,216	1,198	1,367	1,338	12	1,217	(e)	1,371	1,350	20	
1,215	1,214	1,360	1,333	1,220	1,196	1,371	1,346	17	1,213	(e)	1,362	(e)	(e)	
1,214	1,201	1,359	1,328	1,214	1,196	1,375	1,348	29	1,213	1,202	1,369	1,349	35	
1,212	1,199	1,350	1,327	1,213	1,193	1,356	1,348	45	1,214	(e)	1,364	(e)	55	
1,211	1,207	1,348	1,323	1,215	1,214	1,371	1,327	76	1,219	1,202	1,351	1,337	83	
1,215	1,205	1,367	1,350	1,214	1,200	1,376	1,332	93	(f)	(f)	(f)	(f)	100	
1,215	1,203	1,384	----------	1,216	1,196	1,377	1,342	----------	----------	----------	----------	----------	----------	
1,217	1,202	----------	----------	1,216	1,199	1,377	1,341	----------	----------	----------	----------	----------	----------	
1,214	1,198	----------	----------	1,212	----------	1,367	1,338	----------	----------	----------	----------	----------	----------	
1,209	1,202	----------	----------	1,214	----------	----------	1,336	----------	----------	----------	----------	----------	----------	
1,216	----------	----------	----------	----------	----------	----------	1,345	----------	----------	----------	----------	----------	----------	
Average 1,214	1,202	1,359	1,329	1,215	1,199	1,371	1,340	----------	1,215	1,202	1,363	1,345	----------	

[a] From Midland, Calif.
$R_2O_3+MgO+SiO_2=0.5$ percent;
loss on ignition = 1.6 percent.

[b] Prepared by heating $CaSO_4.2H_2O$ of analytical reagent quality for 1 hour at 600° C.

[c] Prepared by heating mixtures of artificial anhydrite (footnote b) and calcium carbonate of reagent quality.

[d] Original composition, calculated.

[e] Not determined.

[f] Not observed, insufficient $CaSO_4$ in mixture to give observable deflection of galvanometer.

a eutectic mixture of the high-temperature form of $CaSO_4$ and CaO. The latter is produced by the decomposition of part of the $CaSO_4$, the SO_3 escaping as a gaseous product. This eutectic is probably low in CaO content, since mixtures originally containing more than 20 percent of CaO did not form sufficient liquid to allow the charge to present the physical appearance of having melted, although as will be seen in table 1 the thermal effect corresponding to the melting of the eutectic was observed. On the other hand, samples originally consisting of pure $CaSO_4$ appeared to have melted when analyses showed that only from 4 to 12 percent of CaO had been formed. Attempts to obtain segments of the liquidus curve failed since no further heat effects were observed in any experiment between the melting of the eutectic and the limit of the furnace, 1,545° C. This was presumably due to the decomposition of the $CaSO_4$, which, on the assumption that the eutectic is low in lime, would have shifted the composition in the direction of high-melting mixtures. It is apparent that a closed apparatus must be used in a precise study of this system. However, it is interesting to note that Grahmann [2], using a 20-g sample of $CaSO_4$, observed melting at 1,450° C and reported this value as the melting point of pure $CaSO_4$. On the basis of this investigation Grahmann's result may be interpreted as representing a point on the liquidus curve, the true melting point being higher.

Although compounds of CaO and SO_3 corresponding to the formulas $2CaO{\cdot}SO_3$ [4] and $3CaO{\cdot}2CaSO_4$ [8] have been reported, their existence was not confirmed in the present work. X-ray patterns were prepared of samples of both natural and artificial anhydrites quenched from temperatures ranging from 1,200° to 1,545° C, and of mixtures of anhydrite and CaO quenched from temperatures between 1,300° and 1,545° C. In only two cases were lines found in the X-ray patterns that did not correspond with lines in the patterns of anhydrite, CaO or $Ca(OH)_2$ (in samples quenched in water or partly hydrated by atmospheric moisture). Two samples of a mixture originally of the proportions $2CaO{:}1SO_3$ were quenched, one from 1,390° C and the other from 1,545° C. On the corresponding X-ray patterns fairly strong lines were found at a position corresponding to an interplanar spacing of 2.12 A and weak lines were found at 0.942 A. In the patterns of other similar mixtures quenched from similar temperatures, no such lines were observed and, in every pattern obtained, all or all but the weakest lines of the ordinary form of anhydrite were found.

V. SUMMARY

The transition of beta calcium sulfate to alpha calcium sulfate occurs at approximately 1,214° C, but the high-temperature form is unstable and cannot be studied at room temperature. A eutectic mixture appears to be formed by CaO and alpha $CaSO_4$ which melts at approximately 1,365° C. The existence of basic sulfates of calcium was not confirmed.

The author acknowledges his indebtedness to Lansing S. Wells for his suggestions and guidance and to Herbert Insley and Howard F. McMurdie, who prepared the photomicrographs and the X-ray patterns.

VI. REFERENCES

[1] Kalousek, Jumper, and Tregoning, Rock Products **44,** 52 (1941).
[2] Grahmann, Z. anorg. Chem. **81,** 257 (1913).
[3] Marchal, J. chim. phys. **23,** 38 (1926).
[4] Zawadski, Kowalczewski, and Zeromski, Roczniki Chem. **8,** 358 (1928).
[5] Masuda, Proc. Imp. Acad. (Tokyo) **8,** 436 (1932).
[6] Carlson, BS J. Research **9,** 825 (1932) RP510.
[7] Rankin and Wright, Am. J. Sci. [4] **39,** 1 (1915).
[8] Curti, Gazz. chim. ital. **68,** 699 (1938).

WASHINGTON, June 24, 1941.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1414

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THERMAL EXPANSION OF CLAY BUILDING BRICKS

By Culbertson W. Ross

ABSTRACT

The coefficients of thermal expansion of 139 bricks were measured over the range −10° to +40° C (14° to 104° F). These bricks included 1 sample of sand-lime, 9 of fire-clay, and 61 of clay and shale bricks. The clay and shale bricks represented a wide range in properties and included samples from various districts in the United States.

The coefficients of 87 percent of the clay and shale bricks were between 5 and 7 millionths per ° C (2.8 to 3.9 per ° F). The average coefficient of the clay bricks was 6.0 (3.3), of the shale bricks 6.1 (3.4), and of the fireclay bricks 3.9 millionths per ° C (2.2 per ° F). No relation was observed between the thermal expansion and the other physical properties of the bricks.

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I. INTRODUCTION

The change in length of building bricks due to temperature changes is one of the factors sometimes blamed for cracking of brick-masonry walls. Inasmuch as a better knowledge of the thermal expansion of bricks should be useful in the study of this and other problems of structural design, measurements have been made of the linear thermal expansion of 139 bricks, representing 1 lot of sand-lime, 9 of fire-clay, and 61 of clay and shale bricks. These bricks, representing the product of various localities in the United States, were available from other investigations and tests and comprised bricks having a wide range in properties. The coefficients of expansion were measured over the temperature range −10° to +40° C (14° to 104° F), or approximately the range to which they might be subjected in structures. The other physical tests which are customarily used as a measure of quality have been made on the bricks as a matter of record and in the hope that there might be some relation between them and the thermal expansion.

Previous tests of the thermal expansion of bricks have usually been made in connection with the study of some other property of the bricks and are not very extensive.

The Watertown Arsenal report of 1896 gives the thermal expansion of 22 clay and shale bricks over the temperature range 33° to 212° F

(approx. 0° to 100° C). The bricks were kept immersed in water, and the changes in length were measured by means of a 6-inch strain-gage reading to 0.0001 inch. The coefficients of thermal expansion ranged from 3.7 to 13.6 millionths per ° C (2.1 to 7.6 per ° F), with an average of 6.3 (3.5). Fifty percent were within the range 5 to 7 (2.8 to 3.9).

Palmer [1] reported tests on six types of clay and shale and two types of fire-clay bricks. A 20-inch Whittemore strain gage was used to measure the length changes in specimens consisting of three bricks cemented together with litharge-glycerin cement. The bricks were measured in a cold room at −8° C and in another room at +25° C. (17.6° and 77° F). Bricks of each type were divided into two classes, one harder burned than the other. The thermal expansion of the harder burned bricks was in general somewhat less than that of the softer bricks. The coefficients of thermal expansion of the clay and shale bricks were between 3.9 and 8.5 millionths per ° C (2.2 to 4.7 per ° F), with an average of 5.6 (3.1). The coefficient for the fire-clay bricks was about 3.7 millionths per ° C (2.1 per ° F).

Ingberg and Foster [2] reported thermal-expansion measurements on 16 hollow clay tile, a material somewhat similar to clay bricks. These measurements were made by the interferometer method and over a much larger temperature range than used in the present investigation. From 0° to 300° C (32° to 572° F), the coefficients ranged from 5.1 to 7.3 millionths per ° C (2.8° to 4.1 per ° F) for the 10 clay and shale tile, with an average of 6.2 (3.4). The range of the coefficients of the six fire-clay tile was from 3.5 to 6.8 millionths per ° C (1.9° to 3.8 per ° F), with an average of 5.5 (3.1).

II. DESCRIPTION OF APPARATUS

The Tuckerman optical strain gage [3] was used to make the thermal-expansion measurements in this investigation. The thermal expansion of the gage was determined by noting the change of the reading with a change in temperature when the gage was mounted on a metal bar, which had been measured from −10° to +40° C in the thermal-expansion section of this Bureau. In the same way, the change in the reading between different temperatures with the gage mounted on a brick gave the difference between the thermal expansion of the gage and brick, and thus the thermal expansion of the brick.

A diagram of the Tuckerman optical strain gage, which also shows the method by which it is mounted on a brick, is given in figure 1. The gage operates on the optical lever principle. A rotation of the stellite lozenge produced by a relative change in length between the gage and the specimen causes the image of the fiduciary point to move on the scale in the autocollimator. The gage is sensitive to a length change of 0.000002 inch. For many of the tests a 4-inch extension bar was added to the gage, giving a 6-inch gage length. For samples which were available only as half bricks, it was necessary to use the 2-inch gage, as shown in figure 1.

The knife-edges of the gages could not be placed directly on the bricks as these contain hard minerals, which would cause wear and

[1] L. A. Palmer, *Volume changes in brick masonry materials*, BS J. Research **6**, 1003 (1931) RP321.
[2] S. H. Ingberg and H. D. Foster, *Fire resistance of hollow load-bearing tile*, BS J. Research **2**, 1 (1929) RP37.
[3] L. B. Tuckerman, *Optical strain gages and extensometers*, Proc. Am. Soc. Testing Materials **23**, pt. 2, 602 (1923).

change the lever arm of the stellite lozenge. Iron plates about 0.1 inch in width were cemented to the bricks with cellulose nitrate cement to provide bearings for the knife-edges. The gage was held on the specimen by a brass ring and screw.

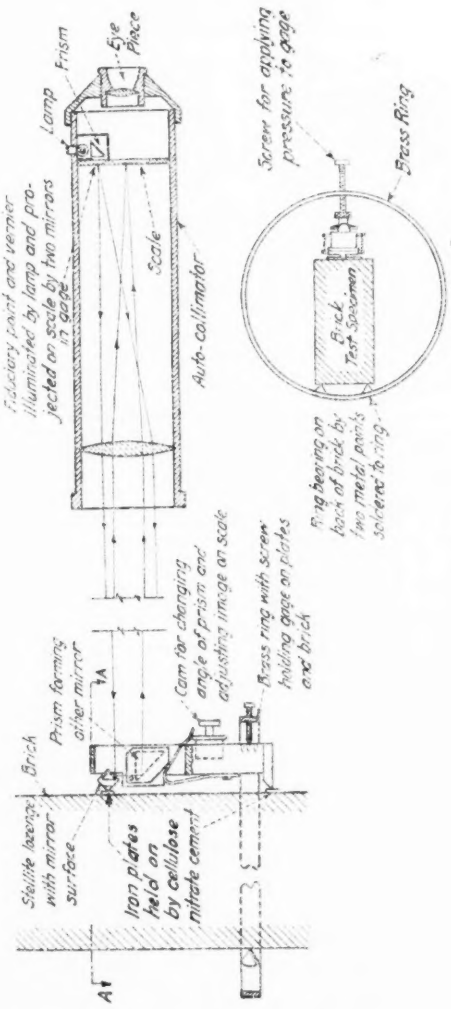
Eye Piece
Prism
Lamp
Fiduciary point and vernier illuminated by lamp and projected on scale by two mirrors in gage
Scale
Auto-collimator
Screw for applying pressure to gage
Brass Ring
Brick Test Specimen
Section "A-A"
Ring bearing on back of brick by two metal points soldered to ring
Cam for changing angle of prism and adjusting image on scale
Brass ring with screw holding gage on plates on brick
Prism forming other mirror
1A
Brick
Stellite lozenge with mirror surface
Iron plates held on by cellulose nitrate cement
A1

FIGURE 1.—*Diagram of the Tuckerman optical strain gage mounted on brick specimen.*

Numerous tests were made, from time to time, on calibrated bars to check the constancy of the gages. The thermal expansion of a 6-inch gage, as determined by seven tests on such a bar, is given in table 1.

TABLE 1.—*Coefficient of thermal expansion of 6-inch gage H, as determined by seven tests on a calibrated bar over a period of 2½ years*

Date	Coefficient of thermal expansion, -10° to $+40^{\circ}$ C
	Millionths per ° C
June 14, 1937	11.78
August 12, 1937	11.76
February 3, 1938	11.78
February 8, 1938	11.78
June 9, 1938	11.81
August 31, 1939	11.77
February 17, 1940	11.79

The coefficients of thermal expansion of an iron bar as determined by four tests with 2-inch gages and of an aluminum alloy bar as determined by two tests are given in table 2. These show the reproducibility of data obtained with 2-inch gages on metal bars which did not require mounting plates.

TABLE 2.—*Coefficient of thermal expansion of an iron bar and of an aluminum alloy bar, as determined by tests with 2-inch gages*

Gage	Coefficient of thermal expansion, -10° to $+40^{\circ}$ C, of an iron bar	Gage	Coefficient of thermal expansion, -10° to $+40^{\circ}$ C, of an aluminum alloy bar
	Millionths per °C		*Millionths per °C*
D	11.38	*D*	22.31
E	11.43	*G*	22.33
F	11.36		
G	11.38		

A sketch of the controlled temperature oven in which the tests were made is shown in figure 2. Approximately 1 watt per °C elevation above room temperature was required to balance the heat loss. The heat input was controlled manually. The copper plates distributed the heat so that, at equilibrium, there was less than 0.1° C difference between the temperatures of the thermometers. The temperature for the lower point of the range was obtained by circulating cold brine through the copper tubes near the top and bottom of the oven.

The temperatures were measured by means of six copper wire resistance thermometers placed in the copper box about the bricks in the locations shown. Their resistance was measured with a Wheatstone bridge and galvanometer. They were calibrated to 0.1° C by means of a six-junction thermocouple and a portable potentiometer after being placed in the oven. The calibration was checked on several later occasions and showed no change as great as 0.1° C.

The gages were read with the autocollimator through holes in the cover of the oven. These holes were normally closed by wooden plugs. The removal of the plugs did not allow enough air to circulate from the room into the oven to cause an observable change in the reading of the gage in the few seconds required for the measurement.

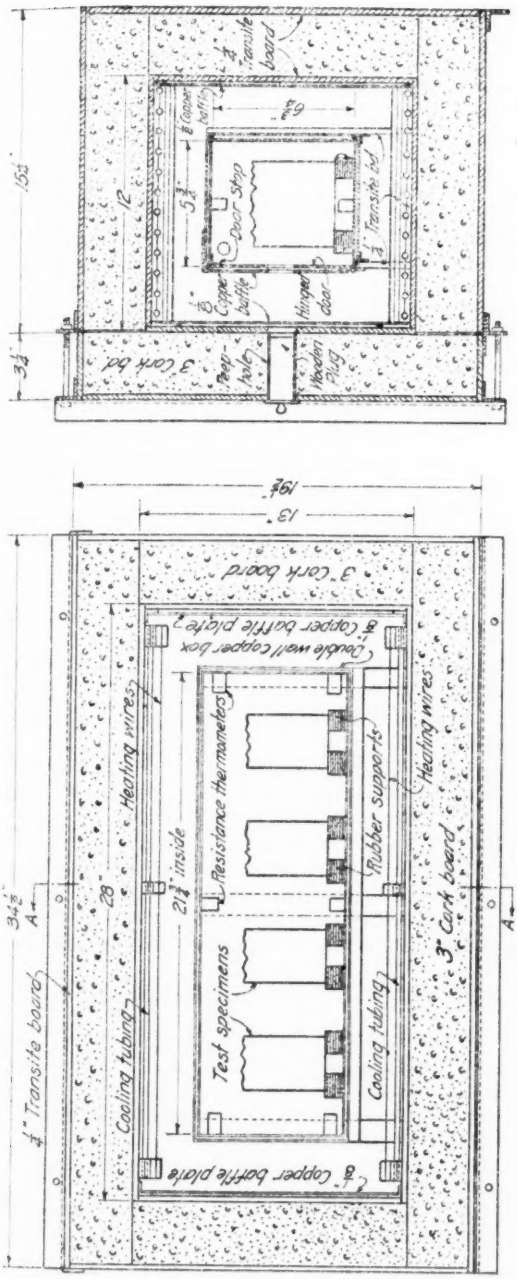

FIGURE 2.—*Diagram of the oven in which the thermal expansion tests were made.*

The bricks were supported in the oven by small pieces of rubber cut from automobile tire inner tubes, which allowed the position of the bricks to be adjusted so that the gages could be viewed through the openings in the oven and helped to prevent vibration from the floor being transmitted to the bricks and gages.

III. TEST PROCEDURE

The bricks were dried at a temperature of 105° to 110° C before the tests. The gages were then mounted on the bricks and the bricks and gages placed in the oven and their position adjusted so that the gages could be viewed through the openings in the door of the oven.

The temperature of the oven was raised to about 40° C and, after the temperature of the oven thermometers became uniform, the readings of the gages were recorded. About 5 hours was required for the temperature to become uniform after the oven had reached the approximate temperature desired. The cooling brine was turned on and the overnight period of 17 hours was allowed for the temperature of the oven to reach the lower point of the range and become uniform, usually at about −10° C. The readings were again recorded and the temperature of the oven raised to 40° C.

The bricks were subjected to two cycles of cooling and heating, giving four values of the thermal expansion. The average of the four values was taken as the value of the thermal expansion for the test. A number of tests were made on each brick.

Different gages usually were used in the different tests of a given brick and the tests on each brick were spread over a considerable period of time as a further check on the constancy of the gages. More tests were made on the bricks tested with the 2-inch gages than on those tested with the 6-inch gages as the data obtained with the shorter gage were less consistent.

After the thermal-expansion tests were completed, the compressive strength, the modulus of rupture, the 5-hour boiling absorption, and the 24-hour water absorption were determined for the bricks in accordance with methods of ASTM Specification C67–39.[4] The compressive strength and modulus of rupture of cored bricks were computed on the basis of the actual sections rather than the gross measurements. The compressive strength and modulus of rupture of bricks 19 to 40 were determined by McBurney and Richmond.[5]

IV. ACCURACY OF THE MEASUREMENTS

The chief limit on the accuracy of the thermal-expansion measurements was a lack of precision in estimating the length of the portion of the bricks within the gage length. Both the iron plates and the cellulose nitrate cement have a higher thermal expansion than the bricks, and considerable uncertainty exists as to the effective point of attachment. The 0.1 inch of the gage length occupied by the plates amounts to 5 percent of the 2-inch and 1.7 percent of the 6-inch gage length. Discrepancies between the values of the thermal expansion from different tests on the same brick were frequently as large as

[4] Am. Soc. for Testing Materials Standards, pt. 2, 104 (1939).

[5] J. W. McBurney and J. C. Richmond—Strength, Absorption, and Resistance to Laboratory Freezing and Thawing of Building Bricks Produced in the United States, Building Materials and Structures (1940), NBS Report BMS60.

this. However, as most of the tests did not give values that differed by these amounts, and since the average of the values from several tests was taken to obtain the final value, it is believed that the error in the final value for the thermal expansion of a brick is substantially less than 1.7 percent for the data obtained with the 6-inch gages and 3 percent with the 2-inch gages. The variation between different tests on metal bars which did not require the mounting plates was much less, as may be seen from table 2.

After the oven temperature was changed, considerable time was required for the temperature of the bricks to approach that of the oven. Since a substantial difference between the temperature of the bricks and that of the gages at the time readings are made might be expected to introduce an error, the time required for the temperatures to approach equilibrium was checked by placing a resistance thermometer in a hole drilled in the center of one of the bricks and comparing its temperature with that of the oven thermometers and the readings of the gages. These data, which were obtained while the temperature was being raised, are given in table 3. In this table the apparent coefficients of thermal expansion of the bricks have been computed, for the conditions at each time interval after 30 minutes, from the change in the readings of the gages and the change in temperature of the oven thermometer which indicated the lowest temperature. This thermometer was located at the center of the bottom of the copper box, and from its location would be expected to give a better indication of the temperature of the bricks than any of the other five shown in figure 2.

TABLE 3.—*Changes in the temperature of the oven thermometers, in the temperature of one of the bricks, and in the readings of the gages as the temperature of the oven was raised from the lower to the higher point of the range*

Time after heat was turned on (min)	Highest of 6 oven thermometers	Lowest of 6 oven thermometers	Thermometer in brick 101	Change of reading of gage *H* on brick 101	Coefficient of thermal expansion[a] of brick 101	Change of reading of gage *F* on brick 122	Coefficient of thermal expansion of brick 122
	°C	°C	°C	*Millionths in. per in.*	*Millionths per °C*	*Millionths in. per in.*	*Millionths per °C*
0	−10.9	−10.9	−10.9	0		0	
30	+3.7	+2.4	−8.0	68		75	
60	25.0	20.9	+1.7	210	5.18	230	4.63
90	41.0	36.2	14.7	317	5.05	353	4.37
120	42.3	39.2	26.5	332	5.15	378	4.32
180	42.4	41.1	36.2	337	5.30	387	4.42
240	42.2	41.5	39.7	339	5.31	390	4.42
330	41.8	41.6	41.0	341	5.28	392	4.39
1,270[b]	38.5	38.4	38.5	321	5.27	368	4.40

[a] From −10.9° C to the temperature given in the third column.
[b] Heating current reduced slightly and oven allowed to stand all night for this reading.

The surprisingly small error caused by the temperature of the bricks, gages, and oven not being equal may be accounted for by noting in table 4 that the thermal expansion of the gages was about twice that of the bricks and that they were mounted on the surface of the bricks where their temperature would be about midway between that of the bricks and that of the oven thermometers. Thus, if the temperature of the oven is 40° C, of the gage 35° C, and of the brick 30° C, and the coefficient for the gage is 12 millionths per °C and for

the brick 6 millionths per °C, both would be 0.000060 inch per inch shorter than they would be if all temperatures were 40° C. There would then be no relative change in length, and the gage would read the same as it would if all the temperatures were 40° C. Several tests were made on other bricks and with the temperature going down as well as up, with similar results. This automatic compensation was not used to shorten the time required for the tests and would be less effective for bricks for which the thermal expansion was substantially different from those of the bricks given in table 3. For most of the bricks it lessens the likelihood of small differences between the temperatures of the bricks and gages, causing errors in the thermal expansions obtained.

TABLE 4.—*Constants a and b for expressing the thermal expansion as a two-term equation in powers of the temperature*

Number of brick	Constant *a*	Constant *b*	Thermal expansion, −10° to +40° C	Number of brick	Constant *a*	Constant *b*	Thermal expansion, −10° to +40° C
	×10⁻⁶	×10⁻⁶	*Millionths per °C*		×10⁻⁶	×10⁻⁶	*Millionths per °C*
53	5.05	0.017	5.55	100	4.80	.012	5.15
54	4.95	.018	5.50	104	5.55	.012	5.90
64	5.20	.013	5.60	105	5.50	.012	5.85
69	5.65	.012	6.00	113	3.55	.011	3.90
70	5.40	.012	5.75	114	3.90	.010	4.20
76	4.85	.011	5.20	115	3.95	.012	4.50
81	4.95	.012	5.30	133	5.95	.013	6.35
82	4.90	.012	5.25	134	6.15	.013	6.55
85	4.65	.013	5.05	135	5.85	.011	6.20
86	4.75	.012	5.10	136	4.95	.012	5.30
89	4.85	.013	5.25	137	11.55	.029	12.40
90	4.45	.015	4.90	138	10.85	.028	11.70
92	2.90	.013	3.30	139	9.40	.026	10.20
94	8.10	.009	8.35				
95	5.50	.013	5.90	Standard bar	11.14	.0132	11.54
				Gage *H*	11.32	.0153	11.78
				Gage *F*	11.42	.0148	11.86

In some of the tests the expansion measured as the temperature increased was substantially different from that as the temperature decreased, as shown in table 5. This might be taken to indicate an irreversible change in the length of the brick due to a change in water content or to the temperature changes. However, as other tests on the same brick frequently did not show this change in length, it probably was due to a slight shifting or creep of the plates on which the gages were mounted rather than to changes in length of the brick. The average of the values from such tests was usually in good agreement with others which did not show this apparent change in length.

The differences between the thermal expansions of the gages, bricks, and calibrated bars, for the small temperature range used in this investigation, are very nearly proportional to the temperature. Since the differential method was used, the variation of the temperature range of several degrees does not affect appreciably the values of the thermal expansions obtained.

TABLE 5.—*Thermal expansion data, −10° to +40° C, for two bricks, with 6-inch gages*

Brick number	121	121	122	122	122
Gage	*H*	*F*	*F*	*H*	*F*
	Change in reading of gage, millionths inch per inch per ° C				
Temperature decreasing	7.41	7.38	7.63	7.53	7.59
Temperature increasing	7.19	7.39	7.49	7.50	7.47
Temperature decreasing	7.39	7.41	7.54	7.52	7.54
Temperature increasing	7.30	7.38	7.49	7.52	7.48
Average	7.32	7.39	7.54	7.52	7.52
Coefficient of thermal expansion of gage	11.78	11.86	11.86	11.78	11.86
Coefficient of thermal expansion of brick	4.46	4.47	4.32	4.26	4.34
Final average		4.47			4.31
Standard deviation		0.01			0.04

There is some evidence in the data that the 2-inch gages gave a value of the coefficient of expansion about 0.2 millionths per ° C higher than that given by the 6-inch gages. Tests were made with both gages on similar bricks, 1 to 5, 6 to 11, and 12 to 18, and both gages were used on the same bricks for the seven given at the end of table 6.

The values of the coefficient of thermal expansion found by means of the 2-inch gages for both halves of the same brick agreed within 0.2 millionth per ° C, except for bricks 12 and 15, which are unusually soft bricks. Of course, there is no reason why the thermal expansions of both halves of a brick should be the same, but the fact that, except for this one type, the independently determined expansions of the two halves agreed so closely leads one to expect that the random error in the values is less than this amount. A systematic error would not be disclosed by this comparison.

TABLE 6.—*Coefficient of thermal expansion of 139 bricks over the temperature range −10° to +40° C. with description and the data for the other physical tests made on the same bricks*

[C, clay; S, shale; F, fire-clay; SL, sand-lime; SM, soft mud; SC, side cut; DP, dry press; EC, end cut; DD, down draft; UD, up draft]

Brick No.[a]	Material	Method of forming	Kiln	Manufacturer's grade name	Locality of production	Compressive strength	Modulus of rupture	5-hour boiling absorption, *B*	24-hour water absorption, *C*	Saturation coefficient (*C*/*B*)	Coefficient of thermal expansion	Number of tests	Root mean square of deviation from mean	Brick No.[a]
						*Lb/in.*²	*Lb/in.*²	*Percent dry weight*	*Percent dry weight*		*Millionths per °C.*		*Millionths per °C.*	
1a	F	SC		Kittanning	Western Pennsylvania			1.8	0.7		*3.2	5	0.08	1a
1b	F	SC			do	12,500	3,100	1.5	.6		*3.1	4	0.05	1b
2a	F	SC			do			1.3	.3		*2.3	8	.08	2a
2b	F	SC			do	15,900	3,100	1.2	.3		*2.2	9	.03	2b
3a	F	SC			do			1.5	.3		*3.3	7	.06	3a
3b	F	SC			do	14,200	3,500	1.4	.2		*3.4	8	.05	3b
4	F	SC			do	20,600	2,500	1.8	.4		3.05	3	.05	4
5	F	SC			do	18,200	2,600	1.4	.3		3.05	1		5
Avg.						16,300	3,000	1.5	.4		*3.1			Avg.
6a	S	SC			Washington, D. C			10.1	6.5	0.64	*6.5	3	0.04	6a
6b	S	SC			do	5,100	1,360	10.7	7.4	.69	*6.3	4	.04	6b
7a	S	SC			do			12.1	8.9	.73	*6.1	2	.05	7a
7b	S	SC			do	4,400	1,180	12.5	9.4	.75	*6.2	3	.11	7b
8a	S	SC			do			10.2	6.8	.67	*6.3	4	.08	8a
8b	S	SC			do	6,200	1,340	9.3	5.1	.55	*6.1	6	.06	8b
9a	S	SC			do			11.8	7.6	.64	*6.3	7	.05	9a
9b	S	SC			do	5,500	1,550	10.8	7.9	.73	*6.3	3	.05	9b
10	S	SC			do	5,500	1,020	12.5	9.7	.78	5.85	3	.07	10
11	S	SC			do	5,800	1,370	12.3	9.3	.76	6.00	1		11
Avg.						5,400	1,300	11.3	8.3	.73	*6.1			Avg.
12a	C	DP			Washington, D. C			19.8	17.2	.87	*7.5	8	0.18	12a
12b	C	DP			do	2,150	130	20.2	17.5	.87	*6.5	4	.21	12b
13a	C	DP			do			19.5	11.6	.60	*6.7	5	.06	13a
13b	C	DP			do	2,070	170	19.1	16.8	.88	*6.6	7	.09	13b
14a	C	DP			do			17.8	14.3	.80	*7.2	5	.08	14a
14b	C	DP			do	2,080	200	19.7	15.7	.80	*7.0	6	.06	14b
15a	C	DP			do			14.5	11.2	.77	*6.9	8	.13	15a
15b	C	DP			do	3,500	570	14.2	10.9	.67	*6.1	7	.06	15b
16	C	DP			do	4,090	480	14.4	12.0	.85	6.45	2	.03	16
17	C	DP			do	2,090	250	18.1	15.4	.85	6.85	2	.01	17
18	C	DP			do	2,560	290	17.6	14.8	.84	6.50	2	.04	18
Avg.						2,600	300	17.5	14.0	.80	*6.7			Avg.

20	C	SC	DD	Select White	Whitewater, Wis	1,900	400	21.1	5.6	0.82	*5.0	4	0.10	20
21	C	SM	Scove	Stock	Detroit, Mich	4,400	500	22.7	18.5	.82	*6.0	4	.02	21
22	C	SM	UD	Select Hard	Kingston, N. Y	6,100	780	16.0	14.9	.78	*6.2	4	.02	22
23	S	DP	UD	Kiln run	Lebanon, N. H	9,000	1,950	7.1	4.9	.41	*5.2	4	.16	23
24	S	DP	UD	do	D'Hamis, Tex	6,800	980	20.8	18.7	.88	*6.0	6	.03	24
25	C&S	DP	Scove	Arch	Pueblo, Colo	5,500	1,050	15.3	12.7	.85	*6.6	6	.07	25
26	S	SC	UD	Picked Reds	Sheridan, Wyo	4,200	320	13.8	11.1	.80	*6.5	4	.05	26
27	C	EC	Dutch	Medium	Pueblo, Colo	7,200	1,370	14.7	12.6	.86	*6.7	4	.09	27
28	S	SC	Tunnel	Common hard	Sharon Hill, Pa	7,400	780	12.1	7.6	.63	*6.2	4	.10	28
29	C	SC		Common	Cleveland, Ohio	6,700	700	11.8	9.3	.79	*6.5	6	.05	29
30	S	DP	DD	Clinker	Richmond, Va	7,030	1,350	11.8	7.5	.66	*5.9	5	.12	30
31	C	SM	Scove	Red Face	Birmingham, Ala	15,800	2,160	7.0	4.1	.59	*4.7	4	.11	31
32	S	SC	DD	Exterior	Detroit, Mich	8,600	2,320	10.8	4.4	.41	*5.7	5	.08	32
33	F	SC	DD	Hard	Alton, Ill	16,700	2,370	3.0	.7	.25	*9.0	5	.08	33
34	C	SC	Dutch	Common	Alliance, Ohio	21,000	2,300	5.4	1.3	.25	*8.7	4	.06	34
35	C	SM	Scove	Black Arch	Baltimore, Md	13,000	2,100	4.2	1.4	.33	*6.9	4	.14	35
36	S	SC	DD	Kiln run	Lebanon, N. H	14,000	2,500	8.6	5.5	.64	*5.3	5	.07	36
37	C	SC	DD	Clinker	Allentown, Pa	12,000	2,030	5.2	2.6	.50	*6.8	6	.16	37
38	C	SM	Scove	Reds	Evansville, Ind	14,100	2,500	3.2	.5	.15	*5.9	3	.04	38
39	C	SM	DD	Clinker	Cleveland, Ohio	10,100	1,700	1.5	.5		*5.3	3	.11	39
40	C	SM	DD	do	New London, Wis	9,500	1,130	15.5	10.7	.69	*6.7	3	.05	40
41a	C	SM	DD	Semiantique	Upper Sandusky, Ohio	16,000	3,200	.8	.2		*6.5	4	.03	41a
41b	C	SM						20.0	15.4	.77	*5.7	3	.07	41b
42a	C	SM				3,700	430	19.3	14.3	.74	*5.7	3	.05	42a
42b	C	SM						18.2	13.7	.75	*5.9	3	.12	42b
avg. c						4,000	890	17.9	13.5	.75	*5.8	7	.13	avg. c
						3,800	660	18.8	14.2	.75	*5.8			avg.
43a	S	SC		Sewer brick				4.5	2.4	.53	*6.5	9	.05	43a
43b	S	SC		do		13,300	3,100	5.0	2.6	.56	*6.4	3	.11	43b
avg.								4.6	2.5	.54	*6.4			avg.
44a	S	SC		Sewer brick				6.1	3.8	.62	*6.6	5	.05	44a
44b	S	SC		do		8,100	1,950	6.0	3.8	.63	*6.6	3	.10	44b
avg.								6.0	3.8	.62	*6.6			avg.
45a	S	SC		Sewer brick				5.5	3.5	.64	*6.5	3	.06	45a
45b	S	SC		do		10,900	3,300	5.2	3.3	.63	*6.7	4	.07	45b
avg.								5.4	3.4	.63	*6.6			avg.
46a	C	Semi-DP			Washington, D. C			12.5	10.1	.81	*6.9	2	.03	46a
46b	C	do			do	4,900	810	12.5	10.1	.81	*6.7	2	.08	46b
47a	C	do			do			11.6	8.9	.77	*6.6	3	.13	47a
47b	C	do			do	5,300	1,060	11.8	9.3	.79	*6.5	3	.04	47b
avg.						5,100	900	12.3	9.6	.79	*6.7			avg.

See footnotes at end of table.

TABLE 6.—*Coefficient of thermal expansion of 139 bricks over the temperature range −0° to +40° C, with description and the data for the other physical tests made on the same bricks*—Continued

Brick No.[a]	Material	Method of forming	Kiln	Manufacturer's grade name	Locality of production	Compressive strength	Modulus of rupture	5-hour boiling absorption, B	24-hour water absorption, C	Saturation coefficient (C/B)	Coefficient of thermal expansion	Number of tests	Root mean square of deviation from mean	Brick No.[a]
						Lb/in.[2]	*Lb/in.*[2]	*Percent dry weight*	*Percent dry weight*		*Millionths per °C.*		*Millionths per °C.*	
48	C	SM		Salmon	New Oxford, Pa.	1,440	165	23.5	14.6	0.62	4.90	2	0.02	48
49	C	SM		do	do	1,130	185	24.7	16.2	.66	5.05	2	.01	49
avg						1,290	175	24.1	15.4	0.64	4.95			avg.
50	C	SC			Baltimore, Md.	7,100	990	12.1	10.0	0.83	6.10	4	0.14	50
51	C	SC			do	10,600	1,200	9.8	7.6	.78	5.75	2	.00	51
avg						8,800	1,100	10.9	8.8	0.81	5.90			avg.
52	C;	SC		Hard	Washington, D. C.	6,900	490	11.1	7.8	0.70	5.75	2	0.06	52
53	C	SC		do	do	7,500	670	12.9	8.9	.69	5.55	2	.01	53
54	C	SC				6,700	650	12.8	8.9	.70	5.50	2	.06	54
avg						7,000	600	12.3	8.5	0.70	5.60			avg.
55	S	DP		Hard	Dallas, Tex.	7,400	820	14.4	12.7	0.88	5.90	3	0.04	55
56	S	DP		do	do	10,100	1,150	13.5	11.8	.87	5.75	2	.10	56
avg						8,700	990	14.0	12.2	0.88	5.80			avg.
57	C	SM	Scove		Detroit, Mich.	4,000	400	21.9	19.3	0.88	5.40	2	0.05	57
58	C	SM	do		do	3,700	430	23.6	20.7	.88	5.70	2	.06	58
avg						3,800	420	22.8	20.0	0.88	5.55			avg.
59	C	DP			Gonzales, Tex.	2,000	480	33.4	27.2	0.81	6.25	2	0.01	9
60	C	DP			do	4,800	850	31.6	26.3	.83	6.90	2	.06	50
avg						3,400	660	32.5	26.8	0.82	6.55			6
61	C	SM			Lancaster, Pa.	4,800	960	16.2	11.7	0.72	5.85	2	0.01	avg.
62	C	EC			Chicago, Ill.	3,500	2,000	14.9	9.0	.60	5.90	2	.04	61
63	C	EC			do	3,300	1,280	19.5	15.6	.80	6.00	2	.08	62
64	C	EC			do	2,600	1,490	14.8	10.4	.70	5.60	2	.02	63
avg d					Chicago, Ill.	3,100	1,600	16.4	11.7	0.70	5.85			64
														avg.

65	C	SM			Hudson Valley, N. Y	2,700	380	25.7	19.7	0.78	5.25	2	0.03
66	C	SM			do	6,200	400	15.5	13.7	.71	5.20	2	.03
avg						4,400	390	21.5	16.7	0.77	6.15		
67	C	SM			Hudson Valley, N. Y	2,840	320	24.3	22.2	0.91	5.95	3	0.04
68	C	SM			do	8,400	970	14.5	11.8	.81	5.75	2	.05
avg						5,600	650	19.4	17.0	0.86	5.85		
69	S	SC			Martinsburg, W. Va	13,200	540	5.2	2.9	0.56	6.00	2	0.02
70	S	SC			do	16,000	1,650	2.6	0.8	.35	5.75	2	.00
71	S	SC			do	13,700	1,910	5.3	2.9	.55	6.05	2	.01
avg						14,300	1,370	4.4	2.2	0.49	5.95		
72	S	SC			Martinsburg, W. Va	6,500	1,130	12.0	9.9	0.82	6.85	3	0.07
73	S	SC			do	6,000	750	13.1	10.9	.83	6.70	2	.04
avg						6,200	930	12.5	10.4	0.82	6.80		
74	C	DP			Washington, D. C	2,740	280	17.0	14.4	0.85	6.30	2	0.01
75	C	DP			do	3,400	320	15.6	12.5	.80	5.65	2	.07
avg						3,100	300	16.3	13.4	0.82	6.00		
76	C	SM		Sand struck	Lebanon, N. H	8,000	1,310	9.6	5.0	0.52	5.20	2	0.02
77	C	SM		do	do	15,600	1,690	8.4	3.7	.44	5.15	2	.01
78	C	SM		do	do	11,600	1,350	8.4	5.5	.65	4.95	2	.02
avg						11,700	1,450	8.8	4.7	0.54	5.10		
79	C	SM		Light burned, sand struck.	Lebanon, N. H	6,300	910	17.0	13.9	0.82	5.10	2	0.02
80	C	SM		do	do	3,400	460	19.4	16.9	.87	5.45	5	.09
81	C	SM		do	do	4,500	810	18.1	14.5	.80	5.30	2	.03
avg						4,700	730	18.2	15.1	0.83	5.30		
82	C	SM		Hard burned, water struck.	Lebanon, N. H	12,700	1,130	5.4	2.7	0.50	5.25	2	0.05
83	C	SM		do	do	16,000	1,920	8.3	5.3	.64	5.10	2	.01
84	C	SM		do	do	13,300	2,330	8.3	5.2	.63	5.25	2	.05
85	C	SM		do	do	15,400	1,140	6.4	1.5	.23	5.05	2	.04
86	C	SM		do	do	14,400	1,390	6.0	1.7	.28	5.10	2	.02
avg						14,400	1,580	6.9	3.3	0.46	5.15		

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See footnotes at end of table.

TABLE 6.—*Coefficient of thermal expansion of 139 bricks over the temperature range −10° to +44° C, with description and the data for the other physical tests made on the same bricks*—Continued

Brick No.[a]	Material	Method of forming	Kiln	Manufacturer's grade name	Locality of production	Compressive strength	Modulus of rupture	5-hour boiling absorption, *B*	24-hour water absorption, *C*	Saturation coefficient (*C*/*B*)	Coefficient of thermal expansion	Number of tests	Root mean square of deviation from mean	Brick No.[a]
						Lb/in.²	*Lb/in.²*	*Percent dry weight*	*Percent dry weight*		*Millionths per °C.*		*Millionths per °C.*	
87	C	SM		Light hards, water struck.	Lebanon, N. H	7,400	1,350	16.5	13.4	0.81	5.00	2	0.01	87
88	C	SM		do	do	7,200	930	17.0	12.9	.82	5.00	2	.06	88
89	C	SM		do	do	7,300	1,070	18.5	15.6	.84	5.25	3	.03	89
90	C	SM		do	do	7,800	790	17.2	14.9	.87	4.90	2	.01	90
avg						7,400	1,030	17.3	14.4	0.84	5.05			avg.
91	F	SC			Kittanning, Pa	18,200	2,700	2.0	0.5	0.25	3.25	2	0.06	91
92	F	SC			do	17,700	2,890	2.3	.7	.29	3.35	2	.01	92
avg						18,000	2,790	2.2	0.6	0.27	3.25			avg.
93	C	SC			Whitewater, Wis	2,000	650	34.4	31.3	0.91	8.10	2	0.04	93
94	C	SC			do	4,100	950	28.6	24.6	0.86	8.35	2	0.04	94
avg						3,050	800	31.5	28.0	0.89	8.20			avg.
95	S	SC		Dealred	Middletown, Pa	7,000	1,100	12.1	10.2	0.84	5.90	2	0.01	95
96	S	SC		do	do	8,000	1,350	10.9	9.5	0.85	5.90	1		96
avg						7,500	1,220	11.5	9.7	0.84	5.90			avg.
97	S	SC		do	Mason City, Ia	17,400	2,300	2.9	1.8	0.62	5.10	2	0.02	97
98	S	SC		do	do	14,200	1,890	10.8	4.9	.45	5.15	1		98
99	S	SC		do	do	13,800	1,430	15.9	10.2	.73	5.15	2	.00	99
100	S	SC		do	do	22,200	1,830	0.3	0.3		5.15	2	.07	100
101	S	SC		do	do	17,200	1,630	8.0	1.5	.19	5.25	2	.02	101
avg						17,000	1,680	7.2	3.7	0.51	5.15			avg.
102	C	EC			Philadelphia, Pa	5,400	1,070	15.4	10.8	0.70	5.90	2	0.05	102
103	C	EC			do	6,100	1,050	15.9	13.2	.70	5.85	1		103
104	C	EC			do	5,200	820	13.6	9.4	.69	5.90	3	.05	104
105	C	EC			do	7,300	950	14.9	10.2	.68	5.85	2	.04	105
avg						6,200	970	15.0	10.4	0.69	5.90			avg.

105	S	L		Sand-lime	St. Paul, Minn.	4,000	640	16.0	11.8	0.73	6.50	2	0.03	105
106	S	L		do	Philadelphia, Pa.	4,100	580	14.2	12.0	.84	10.75	3	.05	106
107	S	L		do	do	4,100	540	13.2	12.0	.91	10.75	3	.05	107
avg.						4,100	580	14.5	11.9	0.83	9.33			avg.
109	F	SC		Enameled	Black Lick, Ohio	21,000	1,600	7.6	6.9	0.91	4.65	3	0.05	109
110	F	SC		do	Momence, Ill.	11,200	950	8.5	4.7	.55	4.10	2	.01	110
111	F	SC		do	Columbus, Ohio	17,300	1,050	6.4	4.2	.66	4.45	2	.01	111
112	F	SC		do	Canton, Ohio	25,000	1,430	5.6	4.7	.84	4.55	2	.00	112
113	F	SC		do	Columbus, Ohio	18,200	2,230	5.1	2.3	.45	3.92	2	.01	113
114	F	SC		do	do	19,800	1,960	4.8	2.2	.46	4.20	2	.03	115
115	F	SC		do	do	21,800	2,245	5.5	3.1	.56	4.30	2	.06	114
avg.a						23,800	2,100	5.2	2.6	0.51	4.25			avg.
116	C	SC				3,800	760	25.8	22.2	0.86	5.90	2	0.04	116
117	S	SC			Mason City, Iowa	10,400	840	15.0	9.1	.61	5.35	2	.00	117
118	C	SM		Reclaimed	Paducah, Kentucky	7,400	860	17.4	14.8	.85	6.30	2	.01	118
119	S	SC			Cleveland, Ohio	12,700	1,750	6.8	2.7	.40	5.95	2	.04	119
120	S	SC			do	5,500	950	12.8	10.4	.81	6.50	2	.04	120
121	C	SM			Baltimore, Md.	2,590	620	17.2	10.2	.59	4.45	2	.01	121
122	C	SM			do	2,100	620	17.0	9.6	.56	4.30	3	.04	122
123	C	SM			do	2,100	490	18.7	11.3	.60	4.30	2	.04	123
avg.d						2,250	580	17.6	10.4	0.58	4.35			avg.
124	S	SC			Martinsburg, W. Va.	19,700	2,360	3.4	2.0	0.59	6.25	3	0.05	124
125	S	SC			do	18,600	1,080	3.2	1.5	.47	6.19	2	.05	125
126	S	SC			do	18,600	2,260	3.4	1.9	.56	6.25	2	.01	126
avg.						19,000	1,890	3.3	1.8	0.54	6.20			avg.
127	C	SC			Baltimore, Md.	5,300	780	13.9	10.2	0.73	4.29	3	0.03	127
128	C	SC			do	5,600	830	13.8	9.6	.70	4.10	2	.11	128
129	C	SC			do	3,600	670	15.5	11.3	.73	4.50	2	.03	129
avg.						4,800	760	14.4	10.4	0.72	4.25			avg.
130	C	DP			Alexandria, Va.	2,170	195	18.2	15.8	0.87	6.25	3	0.01	130
131	C	DP			do	4,120	270	16.6	14.3	.86	6.65	3	.03	131
132	C	DP			do	2,500	169	20.2	18.8	.93	6.45	3	.08	132
avg.						2,900	210	18.3	16.3	0.89	6.45			avg.

See footnotes at end of table.

TABLE 6.—*Coefficient of thermal expansion of 193 bricks over the temperature range −10° to +40° C, with description and the data for the other physical tests made on the same bricks*—Continued

Brick No.[a]	Material	Method of forming	Kiln	Manufacturer's grade name	Locality of production	Compressive strength	Modulus of rupture	5-hour boiling absorption, *B*	24-hour water absorption, *C*	Saturation coefficient (*C*/*B*)	Coefficient of thermal expansion	Number of tests	Root mean square of deviation from mean	Brick No.[a]
						*Lb/in.*²	*Lb/in.*²	*Percent dry weight*	*Percent dry weight*		*Millionths per °C.*		*Millionths per °C.*	
133	S	SC			Martinsburg, W. Va.	14,450	2,100	3.5	1.5	0.43	6.35	2	0.03	133
134	S	SC			do	12,500	2,180	4.5	2.6	.58	6.55	2	.02	134
135	S	SC			do	13,100	2,680	6.9	5.0	.72	6.20	2	.04	135
136	S	SC			do	14,400	2,500	6.4	4.6	.72	5.30	2	.01	136
avg						13,600	2,350	5.3	3.4	0.61	6.10			avg.
137	C	SC			Columbus, Miss.	6,400	870	16.6	11.5	0.69	12.40	3	0.08	137
138	C	SC			do	6,600	900	16.8	12.3	.73	11.70	3	.06	138
139	C	SC			do	5,300	500	16.5	11.8	.72	10.20	3	.10	139
avg						6,100	760	16.6	11.9	0.71	11.45			avg.
4[b]											[e]3.2	3	0.17	4[b]
55[b]											[e]6.0	2	.10	55[b]
91[b]											[e]3.4	3	.17	91[b]
98[b]											[e]5.3	4	.08	98[b]
116[b]											[e]6.1	2	.24	116[b]
117 a[b]											[e]5.3	4	.02	117 a[b]
117 b[b]											[e]5.4	4	.06	117b[b]
120[b]											[e]6.9	2	.26	120[b]

[a] Bricks 19 to 40 are similar to 1 to 22 in the "Water Absorption of Building Bricks." Am. Soc. Testing Materials **36**, pt. 1, 260 (1923). No. 22 is from the same sample as 35, and there is no brick corresponding to No. 17 of the above report. The remainder of the bricks are in the same order as in that report. The compressive strength and modulus of rupture for these bricks were obtained by McBurney and Richmond, Building Materials and Structures (1940) NBS Report BMS60.

Bricks 95 to 96, 97 to 101, 105, 109 to 115, and 119 to 120 were cored.

Bricks 57 and 58 are similar to 20, but of a later shipment.

Bricks 67 and 68 are from a different manufacturer, but of similar raw materials to 65 and 66.

Bricks 72 and 73 are of the same type as 69 and 71, but are not as hard burned.

Bricks 79 to 81 are from the same manufacturer as 76 to 78, but are not as hard burned.

Bricks 87 to 90 are similar to, but not as hard burned as 82 to 86.

Bricks 91 and 92 are similar to 1 to 5, but from a shipment received at a much later date.

Bricks 93 and 94 are similar to 19, but from a later shipment. They have a high lime content.

Bricks 97 to 101 are similar to Nos. 26 to 30 in the report "Water Absorption of Building Bricks." Am. Soc. Testing Materials **36**, pt. 1, 260 (1923).

Bricks 137 to 139 seem to have slag or cinder material mixed with the clay.

[b] Thermal expansion tests were made with both 6- and 2-inch gages. The coefficient obtained with the 6-inch gages and data from the other physical tests are given in this table.

[c] Average is for last 4 items only.

[d] Average is for last 3 items only.

[e] Average is for last 2 items only.

[e] Data obtained with 2-inch gages

V. EXPERIMENTAL RESULTS

Table 6 presents the thermal expansions of the 139 bricks used in this investigation, the data from the other physical tests, and a description of the bricks. Bricks 107 and 108 are sand-lime bricks and, while somewhat extraneous to this investigation, are of interest and have been included. Bricks 19 to 40 are similar to those used in an investigation of different methods of making water absorption tests on bricks.[6] The saturation coefficient is the ratio of the 24-hour water absorption to the 5-hour boiling absorption (see footnote 4). The number of thermal-expansion tests made on each specimen is given, as well as the standard deviation. The values from the different tests with the 2-inch gages were weighted, the weight depending on the spread of the four values of the thermal expansion found with each test.

In order to show the methods used in computing the thermal expansion from the tests and other characteristics of the data, more details are given in table 5 for the two tests with the 6-inch gages on brick 121 and the three tests on brick 122.

Thermal expansions over a large range of temperature are frequently expressed by a two-constant equation in powers of the temperature, such as

$$L_t = L_0 (1 + at + bt^2),$$

in which L_0 is the length of the specimen at the base temperature, L_t is the length at the temperature t, and a and b are constants. An effort was made to obtain the second constant, b, for some of the bricks by taking a reading at a temperature intermediate between the highest and the lowest. This constant is given in table 4 for the bricks on which two tests gave values which differed by less than 0.002×10^{-6}.

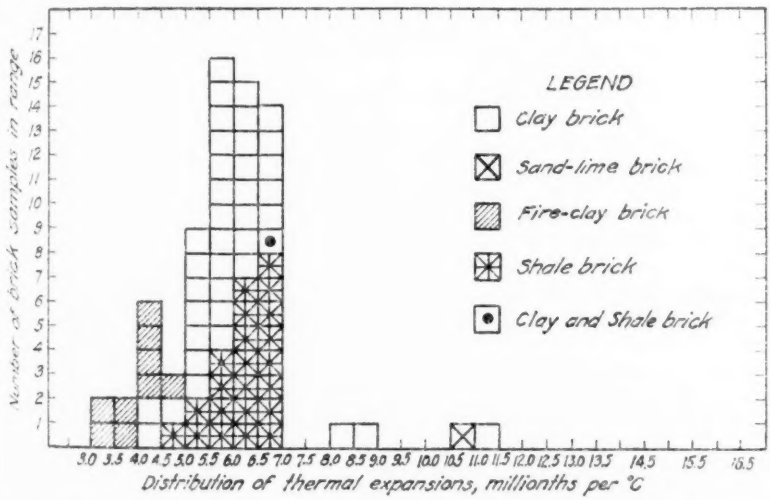
Number of brick samples in range
LEGEND
Clay brick
Sand-lime brick
Fire-clay brick
Shale brick
Clay and Shale brick
3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.5 15.5 16.5
Distribution of thermal expansions, millionths per °C

FIGURE 3.—*Distribution of the thermal expansions of the clay, shale, sand-lime, and fire-clay bricks.*

Figure 3 shows the distribution of the thermal expansions of the bricks. The averages were used, rather than the values for the individual

[6] J. W. McBurney, *Water Absorption of Building Brick*, Am. Soc. Testing Materials **26**, pt. 1, 260 (1923).

bricks, in the cases in which more than one brick from the same lot was tested.

In figure 3 it may be noted that the coefficients of thermal expansion of 54 of the 61 lots of clay and shale bricks, or 89 percent, were between 5 and 7 millionths per ° C. This may be compared with the 22 bricks in the report of the Watertown Arsenal, of which the coefficients for 11 bricks were within this range. Four of the 12 values for clay and shale bricks given by Palmer, and 8 of the 10 for clay and shale tile given by Ingberg and Foster were within the same range. Except for the rather unusual bricks from Whitewater, Wisc. (Nos. 19, 93, and 94) and from Columbus, Miss. (Nos. 137 to 139) the "cut off" at a thermal expansion of 7 millionths per ° C for clay and shale bricks is very sharp.

The few values above 7 and below 5 millionths per ° C among the clay and shale bricks are chiefly limited to the softer clay bricks (5-hour boiling absorption above 14 percent).

The thermal expansions of the fire-clay bricks showed some tendency to decrease with increasing hardness, but the samples are scarcely numerous or representative enough to draw any conclusions on this point.

The thermal expansion of the clay and shale bricks was compared in turn with the compressive strength, modulus of rupture, 5-hour boiling absorption, 24-hour water absorption, and saturation coefficient. No correlation was found between the thermal expansion and these properties, and, even among bricks from the same shipment, there was no consistent tendency for the thermal expansion to increase or decrease with differences of hardness of burning, as indicated by the above physical properties.

The distribution of the thermal expansions with different methods of forming was studied, but nothing significant was found. The only two types of bricks having coefficients above 7 millionths per ° C were both side-cut clay bricks.

The probable error, or rather the probable difference between the thermal expansion of an unknown sample of bricks and the arithmetic mean, has been computed on the basis of the tests reported in this paper and is given in table 7. The probable error for the clay and shale bricks and the clay bricks is larger, chiefly owing to the large departure of the coefficient for bricks numbered 137 to 139 from the mean.

TABLE 7.—*Probable error if the arithmetic mean of the coefficients of thermal expansion is assumed as the coefficient of a brick for which the coefficient is unknown*

Types of brick	Number of lots	Arithmetic mean	Probable error
		Millionths per °C	*Millionths per °C*
Clay and shale	61	6.1	0.7
Clay and shale with 5-hour boiling absorptions less than 14 percent	32	6.0	.4
Clay	38	6.0	.5
Shale	22	6.1	.4

VI. CONCLUSIONS

1. The average values of the coefficients of thermal expansion, their range, and the number of samples tested for different types of clay bricks are given in table 8. For comparison, similar data are given from previous investigations.

TABLE 8.—*Average coefficient of thermal expansion (in millionths per °C) of different types of clay bricks from this and previous investigations*

[The values in parentheses are in millionths per °F]

Types of clays	Number of specimens	Average coefficient of thermal expansion	Range of coefficient of thermal expansion
PRESENT PAPER (BRICKS) −10° TO +40° C (14° TO 104° F)			
Surface clay	80	6.0(3.3)	4.2 to 12.4 (2.3 to 6.9)
Shale	41	6.1(3.4)	4.7 to 6.8 (2.6 to 3.8)
Fire-clay	15	3.9(2.2)	3.0 to 4.6 (1.7 to 2.6)
PALMER (BRICKS) −8° TO 25° C (18° TO 77° F)			
Surface clay	6	6.6(3.7)	4.7 to 8.5 (2.6 to 4.7)
Shale	4	4.8(2.7)	4.1 to 5.2 (2.3 to 2.9)
Fire-clay	4	3.7(2.1)	3.6 to 3.8 (2.0 to 2.1)
INGBERG (HOLLOW TILE) 0° TO 300° C (32° TO 572° F)			
Surface clay	4	6.2(3.4)	5.1 to 7.3 (2.8 to 4.1)
Shale	6	6.1(3.4)	5.7 to 6.9 (3.2 to 3.8)
Fire-clay	6	5.5(3.1)	3.5 to 6.8 (1.9 to 3.8)
WATERTOWN ARSENAL (BRICKS) 0.6° TO 100° C (33° TO 212° F)			
Clay and shale	22	6.3(3.5)	3.7 to 13.6 (2.1 to 7.6)

2. The coefficients of thermal expansion of 89 percent of the clay and shale bricks were between 5 and 7 millionths per ° C (2.8 and 3.9 per ° F), the average being 6.1 (3.4). The value, 6 millionths per °C (3.3 per ° F), is a good value to assume for the thermal expansion of clay and shale bricks, the probable error, as computed from the data of this paper, being about 0.7 millionth per °C (0.4 per °F). Of course, if an accurate knowledge of the thermal expansion of any bricks is desired, the above assumption could scarcely be substituted for an actual test.

3. There was no significant difference between the average thermal expansion of the clay and shale bricks. The few values of the coefficient above 7 and below 5 millionths per ° C are chiefly limited to the softer clay bricks (5-hr boiling absorption above 14 percent).

4. The thermal expansion of the fire-clay bricks was much lower than that of the clay and shale bricks. The number tested, however, was scarcely large enough, nor were the bricks representive enough to allow definite conclusions to be drawn as to the thermal expansion of other fire-clay bricks.

5. There was apparently no significant correlation between the thermal expansion and the other physical properties of clay and shale bricks which are customarily measured as tests of quality, and even among bricks from the same shipment there was no consistent tendency for the thermal expansion to either increase or decrease with differences of hardness of burning.

WASHINGTON, June 18, 1941.

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